

LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
Faculty of Technology
Degree Programme in Technomathematics and Technical Physics

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**KELVIN PROBE FORCE MICROSCOPY (KPFM) CHARACTERIZATION OF LANTHANUM LUTETIUM
OXIDE HIGH-K DIELECTRIC THIN FILMS**

Examiners: Professor Erkki Lähderanta
 C Sc. Mikhail Dunaevskiy

ABSTRACT

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Kelvin Probe Force Microscopy (KPFM) characterization of lanthanum lutetium oxide high-k dielectric thin films

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69 pages, 48 figures, 4 tables and 2 appendices

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Lanthanum lutetium oxide (LaLuO₃) thin films were investigated considering their perspective application for industrial microelectronics. Scanning probe microscopy (SPM) techniques permitted to visualize the surface topography and study the electric properties. This work compared both the material properties (charge behavior for samples of 6 nm and 25 nm width) and the applied SPM modes.

Particularly, Kelvin probe force microscopy (KPFM) was applied to characterize local potential difference with high lateral resolution. Measurements showed the difference in morphology, chargeability and charge dissipation time for both samples. The polarity effect was detected for this material for the first time. Lateral spreading of the charged spots indicate the diffusive mechanism to be predominant in charge dissipation. This allowed to estimate the diffusion coefficient and mobility. Using simple electrostatic model it was found that charge is partly leaking into the interface oxide layer.

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Pavel Geydt

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Tarkastajat: Professori Erkki Lähderanta
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Lantaani-lutetium-oksidihiutkalvoja (LaLuO_3) tutkittiin erityisesti niiden käytettävyyden kannalta teollisessa mikroelektronikassa. Pyyhkäisymikroskopian (SPM) avulla voitiin kuvantaa pinnan topografiaa ja tutkia sen sähköisiä ominaisuuksia. Työssä vertailtiin materiaalin ominaisuuksia (varauskäyttäytymistä 6 nm ja 25 nm leveillä näytteillä) sekä myös käytettyjä SPM:n eri toimintatiloja.

Erityisesti käytössä oli kelvin probe force -mikroskopia (KPFM), jolla tutkittiin paikallisia potentiaali-eroja tarkalla sivuttaistarkkuudella. Mittauksissa havaittiin eroja morfologiassa, varautuvuudessa ja varauksien haihtumisessa molemmissa näytteissä. Polaarisuusilmiö havaittiin ensimmäistä kertaa tällaisissa näytteissä. Jännitepisteiden sivuttainen leviäminen viittaa hallitsevien mekanismien olevan diffuusiivisia. Yksinkertaisen elektrostaattisen mallin avulla huomattiin varauksien osittain vuotavan rajapintakerrokseen.

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I am pleased to thank people who influenced on my interest in the subject of this Master's Thesis. Since I was always keenly interested in the natural sciences, the work in this area has been for me a truly exciting and meaningful experience. I tried with all diligence to understand the problems of Scanning Probe Microscopy and found the prospects for further fruitful research in the field of physical science.

First of all, I want to thank my supervising Professor Erkki Lähderanta for his help in choosing a topic, support at all stages of the Diploma Thesis and for the possibility to study at Lappeenranta University of Technology. Without him, this work would have been impossible.

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Lappeenranta, May 2013

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Table of Contents

1. Introduction	8
2. Semiconductors background	11
2.1. Semiconductor materials and memory devices	11
2.2. High-k dielectrics. Models of charge dissipation.....	12
2.3. Properties and features of LaLuO ₃	14
3. Methodical Section	15
3.1. Scanning Probe Microscopy (SPM), fundamental and classification.....	15
3.2. Atomic Force Microscopy (AFM), main components and principle of operation	16
3.2.1. Electric Force Microscopy (EFM)	25
3.2.2. Kelvin Probe Force Microscopy (KPFM)	27
3.2.3. Force gradient mode in Kelvin Probe Microscopy (KPFGM)	28
3.3. Nanolithography of charge	30
3.4. State-of-the-art systems for SPM	31
3.4.1. "NT-MDT NTegra AURA" device features	31
3.4.2. "BRUKER Multimode 8" device features	32
3.5. Advances in SPM equipment and techniques.....	32
3.6. Software for data and image processing	34
4. Experimental Part.....	35
4.1. LaLuO ₃ thin films.....	35
4.2. Sequence of the measurement	37
5. Results	44
5.1. Topography	44
5.2. Electrical charge behavior.....	45
5.2.1. Electrical chargeability	45
5.2.2. Limiting potential of charging.....	49
5.2.3. Induced charge relaxation time.....	50
5.2.4. Temperature dependence	53
5.2.5. The effect of polarity of charge	56
5.2.6. Force gradient measurements	57
5.3. Nanolithography observations.....	59
Conclusions	61
Summary	63
References	66
Appendices	

List of Abbreviations

AFM	Atomic Force Microscopy; Atomic Force Microscope (device)
ALD	Atomic Layer Deposition
CET	Capacitance Equivalent Thickness
CPD	Contact Potential Difference
DFL	Deflection signal difference between top and bottom halves of the photodiode
EEPROM	Electrically Erasable Programmable Read-Only Memory
EFM	Electric Force Microscopy
FWHM	Full Width at the Half Maximum of signal
IL	Interface oxide Layer
KPFGM	Kelvin Probe Force Gradient Microscopy (KPFM FM)
KPFM	Kelvin Probe Force Microscopy (Amplitude Modulation)
LF	Difference signal between left and right halves of the photodiode
MAG	Magnitude of AFM probe oscillations in Semicontact mode
MBE	Molecular Beam Epitaxy
MOSFET	Metal-Oxide-Semiconductor Field Effect Transistor
NROM	Nitride Read Only Memory
PLD	Pulsed Laser Deposition
QDs	Quantum dots
SHINOS	Silicon Hi-k Nitride Oxide Silicon
SONOS	Silicon-Oxide-Nitride-Oxide-Silicon
SP	Surface Potential (do not confuse with “SetPoint” which is system parameter)
SPM	Scanning Probe Microscopy
STM	Scanning Tunneling Microscopy
UHV	Ultra High Vacuum

List of Symbols

D	diffusion coefficient
d	width of the dielectric layer
E	electric field
F	force applied to the tip
f	resonant frequency
k	dielectric constant
k_T	cantilever's stiffness
L	lateral size of the charged spot
Q	quality factor of the cantilever oscillations
R	tip radius
t	charging duration
τ_{rel}	relaxation time
U	potential difference
w	bending frequency
z	loftiness
μ	mobility
ϕ	work function of the material
λ	numerical coefficient for different vibrational modes
$\Delta\varphi$	phase shift

1. Introduction

Silicon Integrated Circuit (IC) technology has rapidly developed, driven by the continuous increase in device functionalities. Facing the growing demand in computational performance of microchips, the more effective semiconductor devices are required. While crystal size has been decreasing in last four decades, at the same time number of transistors per crystal is growing intensively. Thereby the transistors performance is satisfying the Moor's Law.

Nowadays the size of transistor nanoelements is on industrial range of recently designed and fabricated 22 nm devices (produced from 2012). But it is known that size decreasing results in undesirable heating. Furthermore, a size less than 5 nm for transistors is unachievable due to quantum restrictions and emerging exponential losses of electrical current. The idea of decreasing voltage seems not applicable because voltage has a predicted minimum of 0.2 V.

Second solution is in the increasing of the dielectric "width" to prevent the formation of undesirable capacity on the gate. That's why huge interest has turned to materials with high values of dielectric permittivity k . High- k is the only viable solution according to Semiconductors Roadmap Reports and these materials will be viable in few years outlook.

While recent processors technology maintained by the Intel Corporation inclined to application of hafnium compounds (HfO_2 , $k = 25$), according to S. Sze the needs for computing (processors) and memory (RAMs) applications might be distinguished. A possible solution for rapid memory applications can be found in transistors with floating gate. In these structures, the high- k dielectric is used to make the gate "thicker".

The search for materials with high dielectric permittivity still continues: there are tens of materials with giant k values up to 10^4 , however such materials are not suitable for ICs from the viewpoints of energy band structure and technological interaction with Si wafer. Thus, the record values are held by the Sc- and La-oxides (LaLuO_3 , $k = 32$). These leading high- k semiconductors are produced mainly by methods of ALD, PLD and MBE.

To characterize the material as a prospective dielectric for industrial nano small transistors, one should take into account such properties as: parameters of its interaction with Si-wafer, surface adhesion, ability to be introduced to the surface, thermal and chemical stability, and the material should have fine morphology without defects. Hence, comprehensive studies are needed to define the desirable materials.

KPFM seems to be appropriate technique for such investigations. It allows to study the local potential with both accuracy of potential and high lateral resolution. Due to the two-pass technique, the surface topography and surface potential mapping are obtained simultaneously. Growing number of papers concerned with fundamentals of KPFM and its application for research of electrical properties of semiconductors proves its significance.

Despite the fact that dielectric constant of LaLuO_3 is record high, which is believed to be essential for gate oxide, experimental data revealing its surface electrical properties is missing. One can find only literature of LaLuO_3 growth conditions, crystal structure and morphology, but no available data of chargeability, surface potential and charge carriers mobility, which are necessary for industrial applications.

Due to the prospective properties of LaLuO_3 , the desired study was carried out. Thin films of LaLuO_3 : 1) 6 nm obtained by MBE and 2) 25 nm obtained by PLD (at 450°C), were investigated in idea of possible semiconductor application. It was presumed to measure surface morphology and electrical properties, compare the methods of growth of such films and to determine possibility of nanolithography for LaLuO_3 .

Therefore **the motivation** of this work was to investigate the properties of high-k dielectric thin films of LaLuO_3 by means of Kelvin Probe Force Microscopy, i.e. merging both the perspective material and method of study. Second interest was in finding capabilities of certain SPM modes (e.g. AFM, KPFM, KPFGM) in such investigation. For this purposes the NT-MDT NTegra Aura system was used. This device allowed combining the Contact/Semicontact AFM topography measurements with KPM modes, namely force mode and force gradient mode.

The chosen technique and device permitted the accurate study of surface properties, however the application of such system put definite **restrictions** to our experimental conditions. Limitations and inaccuracies can be distinguished to six main categories:

- device features (creep of piezo ceramics; system background noise and time of scanning)
- software used (mainly, feedback delay and methods for data processing)
- pumping system limitations (only medium vacuum of $2 \cdot 10^{-5}$ bar is possible to reach, which causes limitation of the quality factor Q for cantilever's tip oscillation and water film of few nm thickness existing on the sample's surface)
- cantilever and tip properties (large size of the cantilevers surface lead to an additional electrical interaction with the surface; the tip form is not clearly defined at the same time with the tip radius, which can lead to convolution effects and restrictions of the lateral

- resolution, found at best on device used as one nm in AFM, tens in KPFGM and about hundred in KPFM; tips have certain range of softness; applied voltage was limited by 10 V)
- operator's capabilities (time of the switching the modes and subjective image processing)
 - sample's features (defects usually reveal in topography or surface potential mapping; softness/stiffness of the surface cause restrictions for the impact force and demonstrate both scrapping effect and rip-offs, driving convolution and extra capacity).

It should be mentioned that all these listed items have been noticed in our study.

The experiment and data processing should be considered and planned on the basis of the literature concerned with issue and all the mentioned restrictions. Therefore, the work resulted in this **Master's Thesis is organized as follows:**

- In chapter Semiconductors background, the specific semiconductor properties of high-k materials are described and compared with the LaLuO₃.
- In chapter Methodical Section, the classification and features of different SPM modes are given. The applicability of the equipment used for the measurements is described in details from the structure of the piezo scanner to the abilities of certain modes. The KPFM is discussed both with details of gradient mode KPFGM. The Nanolithography of charge is overlooked since it is itself the technique of charge injection in this work. Finally, the software and future prospects of the study, from positions of SPM and samples behavior are monitored.
- In chapter Experimental part, information about the samples used in our research with methods of growth (which seem valuable in case of found undesirable surface defects) is given. As this work has the methodical value, the SPM and particularly KPM measurements are described step by step.
- In chapter Results chapter, the essence of the research is presented by the discussion of the measurements.
- In Conclusions, the obtained results of parameters and theories are combined by the statements and proposals, followed by the Summary part, where the entire work for purposes of the Master's Thesis is surveyed with justification of the obtained results and ideas for future studies.

2. Semiconductors background

Storing and processing the data can be claimed as main backbones for "21 Century of information". Memory devices are required to perform these basic operations, and they are recently based on the transistor's technology. This semiconductor device is operating with gate, drain and source as main constituents [1]. Since charges are stored in nano small volume, precise methods of their investigation are needed, e.g. local potential measurements.

2.1. Semiconductor materials and memory devices

For instance, one of the most widely used types of semiconductor memory is flash memory (EEPROM): data is retained for long period of time by transistors, which include the data-saving material under the gate (Figure 1). The operational principle is based on injection of electrons by Tunneling mechanism into the floating gate [2]. Since electrical charge is retained inside the gate, it switches the transistor into nonconductive state corresponding to the logical 0. When reverse Voltage is applied to the control electrode of such transistor, the electrons are migrating back to the silicon and create the conductive channel corresponding to logical 1.

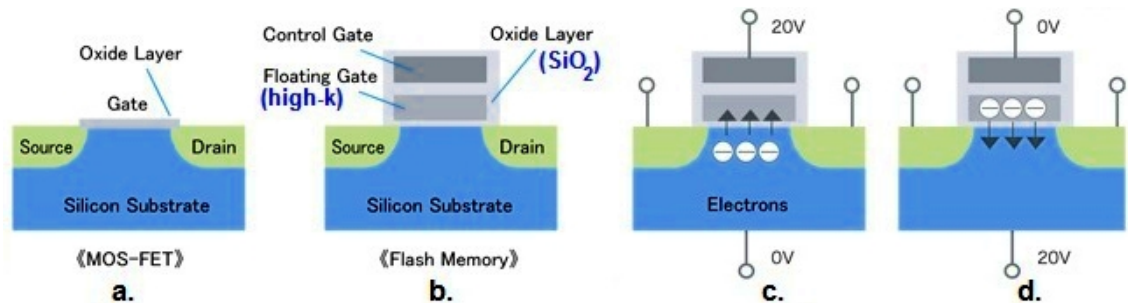


Figure 1. a. MOSFET and b. flash memory construction. c. Write operation: voltage applied to the control gate causes a tunnel current to flow through the oxide layer, thereby injecting electrons into the floating gate. d. Erase operation: voltage applied to the silicon substrate releases the electrons accumulated at the floating gate [Image courtesy of TDK® Corp.].

Reducing the size of the elements, as another trend of high technology, leads to losses of current through the thin gate dielectric layer. According to International Technology Roadmap for Semiconductors reports and recent manufacturing technologies, the silicon dioxide is relic since 2008, and enhancement of materials with larger value of relative permittivity is mentioned as one of the way to overcome the size limits.

It is worth mentioning that even in transistors with another operating principles, e.g. NROM, SHINOS and SONOS structures, electrons are stored in localized position, preserving a bit of

information [3]. These technologies are using mainly Si_3N_4 as a gate dielectric, however the search for suitable materials still continues. The material should provide significant density of charges per nano size local volume.

2.2. High-k dielectrics. Models of charge dissipation

Hafnium compounds are used for processors of 22 nm technology by Intel Corporation in 2013 [4]. Hafnium oxide (HfO_2) satisfies the essential criterions for prominent high-k semiconductor oxide, it is the most used and studied high-k. The requirements of a new oxide are [5]:

- 1) k value must be high enough to be used economically for a reasonable number of years.
- 2) The oxide is in very close contact with the Si channel, thus it must be thermodynamically stable with Si.
- 3) The oxide must be kinetically stable, and able to be processed at 1000°C at least for 5 seconds (in present process flows).
- 4) The oxide must act as an insulator, by having band offsets with Si of over 1 eV to minimize carrier injection into its bands.
- 5) The oxide must form a good electrical interface with Si.
- 6) The oxide must have few bulk electrically active defects.

New candidate for gate oxide is required since 2009, despite the high k of Hf and HfO_2 :

Table 1. Comparison between semiconductors for probable replacing of SiO_2 [5].

	k	Gap (eV)	CB offset (eV)
Si		1.1	
SiO_2	3.9	9	3.2
Si_3N_4	7	5.3	2.4
Al_2O_3	9	8.8	2.8 (not ALD)
Ta_2O_5	22	4.4	0.35
TiO_2	80	3.5	0
SrTiO_3	2000	3.2	0
ZrO_2	25	5.8	1.5
HfO_2	25	5.8	1.4
HfSiO_4	11	6.5	1.8
La_2O_3	30	6	2.3
Y_2O_3	15	6	2.3
a- LaAlO_3	30	5.6	1.8
LaLuO_3	32	5.2	2.1

Besides the mentioned parameters, the locality of charge can be considered to be necessary for storing the data in SONOS and NROM technologies. The locality can be measured by the

charge dissipation in the thin films by the measurements of surface potential. However, precise device is required to track charge behavior: position, migration and dissipation.

Three main mechanisms are discussed to explain the charge dissipation [6, 7]:

1) Charge leakage into the conductive silicon wafer. This mechanism is driven by Tunneling effect. The total injected charge Q is exponentially decreasing in time domain and observed by decrease of local potential. Q is also called "integral charge" since it is calculated as the integral of surface profile curve multiplied by surface area of the local charge.

2) Charge drift. It is described as the Coulomb repulsion of charges of same sign. This causes lateral drift current $j_{drift} = \rho \cdot \mu \cdot E$. The total charge is not changing, but the same time local potential is falling down concurrently with lateral widening of charged spot.

3) Diffusion mechanism. This mechanism of charge dissipation can be described as random walk of charges via trapping centers. Total charge Q do not change, diffusion current is given by formula $j_{diff} = -D \cdot \nabla \rho$, where D is diffusion coefficient and ρ is the density of charges. Observed lateral widening for charged spot is proportional to $t^{0.5}$.

Results for ternary rare oxides (e.g. DyScO₃ and GdScO₃) have shown its promising conformity for abovementioned six requirements with observed $k \approx 20 - 35$. The studied Sc- based oxides has shown even better values of $k \approx 28 - 33$ with more appropriate morphology and energy band structure [8 - 11]. Measurements of LaScO₃ has shown its considerable locality in range of hundred nm, though it is less than lateral size observed for SiO₂ with embedded Si nanocrystals (material SiO₂ nc-Si), which was measured at best to be nearly 25 nm [11].

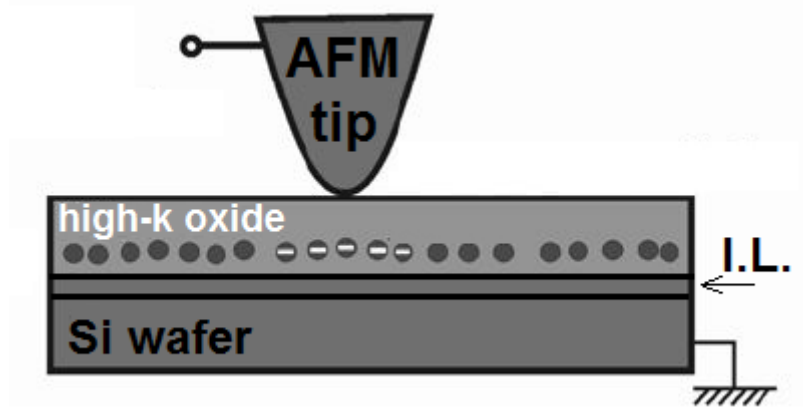


Figure 2. Experimental scheme of charge measurements by AFM. Injection, scanning [7].

Further results for LaScO_3 have shown the predominant mechanism of charge leakage, when local charge observations were performed by Atomic Force Microscope. The scheme of experiment is shown on Figure 2. A sharp tip of a Microscope is injecting charge by applying bias voltage. Then AFM tip is scanning the surface to study the map of surface potential, thus obtaining the values of potential decrease and lateral spreading with high accuracy.

It must be noted that tunneling was claimed as the main mechanism for LaScO_3 , however the lateral widening was found. It was explained by diffusion inside the interface layer (IL). The role of this oxide layer remains unclear. In literature was discussed one more La based oxide LaLuO_3 and it has shown even higher value of dielectric constant, $k = 32$. However experimental data related to high-k applications is not available and its systematical study is required according to authors of [8].

2.3. Properties and features of LaLuO_3

LaLuO_3 oxide thin films made of a stoichiometric ceramic target by Pulsed Laser Deposition (PLD) has proven [8] its appropriate morphology of nearly 2 nm roughness (AFM), stoichiometry by X-Ray reflectometry (XRR) $\text{La:Lu} = 1:1.1$ and dependence of dielectric constant to the growth conditions [8, 11]. For instance the thermal method (PLD) has shown higher results for $k = 32$ in nearly two times in comparison to the value for the film grown in room temperature ($k \approx 17$). Both internal photoemission (IPE) and photoconductivity (PC) measurements have shown the value of energy barrier 5.3 eV. The Capacitance-Voltage (C-V) measurements have shown low leakage current density, depending on the film thickness, which resulted in calculating the Capacitance Equivalent Thickness (CET) giving the $k = 32$.

Further study of electrical properties of the LaLuO_3 dielectric thin films was concluded as significant.

3. Methodical Section

3.1. Scanning Probe Microscopy (SPM), fundamental and classification

Scanning probe Microscopy is the type of microscopy techniques, in which a physical probe is scanning the sample's surface. The start of this microscopy was established by foundation of the Scanning Tunneling Microscope (STM) in 1981. In STM surface topography (map of the heights with roughness) is measured by the tunneling current in vacuum between probe and conductor [12]. Since many opportunities were presumed for technology of semiconducting materials and insulators, structure of the microscope was developed to the construction with small reflective cantilever plate, which reflected the laser light onto the photo detector.

Working principle became independent from conductivity, instead of it the Van der Waals attractive-repulsive interaction revealed topography for solid materials and even liquids. This construction, including the photo detector and cantilever is called Atomic Force Microscope (AFM, 1986) [13]. Since these two devices provided significant enhancement in studying of surface properties, their developers Binnig and Rohrer received Nobel Prize in 1986.

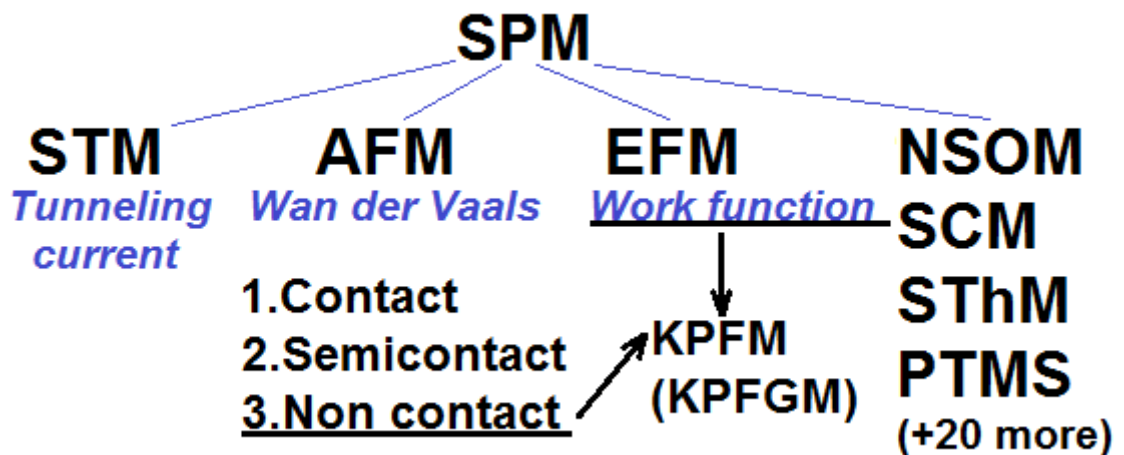


Figure 3. Types of Scanning Probe Microscopy. Family of KPM methods.

For the last three decades at least 30 other types of Scanning Probe devices have appeared. They distinguish the information source: light radiation, noise, capacity etc. Each of them permit measurement of specific forces (e.g. electrical forces, magnetic interaction). The basic classification for SPM methods is given in Figure 3. It is impractical to discuss all the possibilities of SPM, thereby this Thesis is oriented on special variety of techniques and modes, i.e. AFM, KPFM and KPFGM (another name is KPFM Frequency Modulation).

3.2. Atomic Force Microscopy (AFM), main components and principle of operation

Atomic Force Microscopy (AFM) is an experimental method to study local properties of the surface, based on Van der Waals interaction between a solid probe tip and the sample surface. The first Atomic Force Microscope was invented in 1986 by G.Binnig, K.Quate and K.Gerber. Due to nanometer sharpness of the tip probe, the AFM has nanometer and even sub-nanometer atomic resolution [13, 14]. Depending on the type of tip-sample interaction it becomes possible to measure the local parameters of topography, surface potential, mechanical properties (stiffness, adhesion, friction), magnetic properties etc.

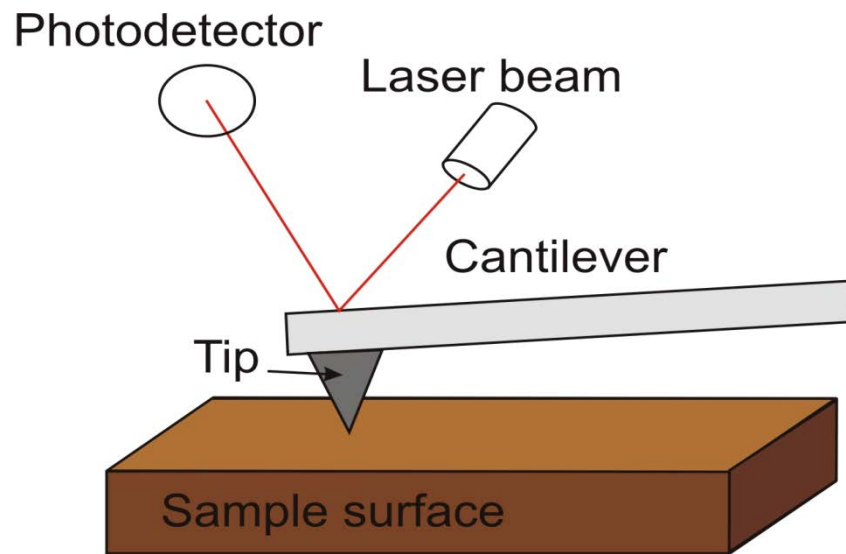


Figure 4. Operational principle of AFM [Image courtesy of Connexions®, Rice University, USA].

The operational principle of the AFM is based on mechanical force between the probe and the surface, and the measured system parameters are describing the relief (as opposed to the STM, MSM and other techniques). A special detecting console is used to register roughness. It is called “cantilever”, and include sharp tip at the end (Figure 4). Van der Waals interaction defines the certain force acting the tip (corresponding to the SetPoint), however surface roughness creates additional force, which results in bending of the cantilever. Then bending angle is detected on the photo detector by shift of laser beam and recorded by system at each point. Finally, tip’s trajectory profile is displayed as the scanned line.

Probe-surface interaction is described by attraction-repulsion model. When the tip is close to the surface, then it is engaged in complex power interaction due to the elastic properties of atomic shell [15]. It is possible to distinguish three areas of elastic impact, depending on value of applied force as described in Figure 5.

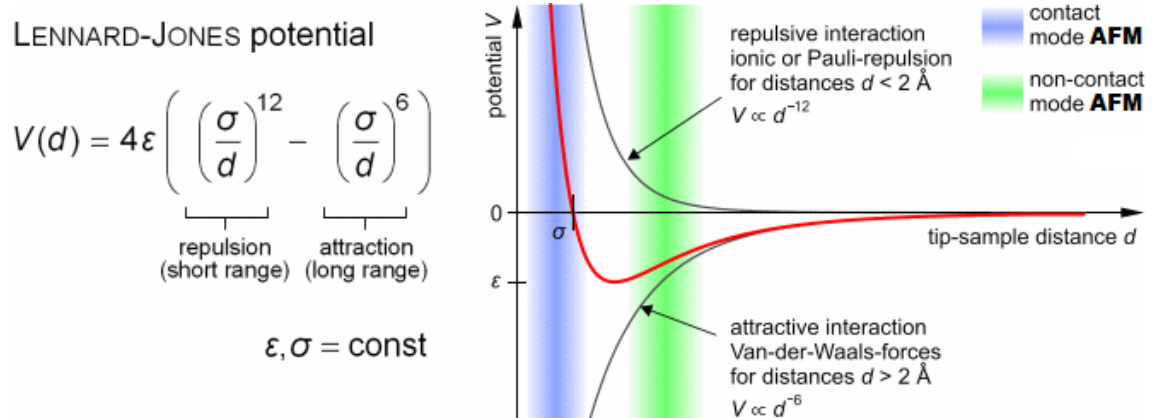


Figure 5. Lennard-Jones potential: equation and curve [15]. [Image courtesy of Soft Matter Physics Division, University of Leipzig, Germany]

This Figure represents graph of the Lennard-Jones potential. In the left part of the curve can be seen a sector of Contact Mode. The probe is in direct contact with the sample - it pushes the surface. The strength of applied pressure is given by the system as the “**SetPoint**” parameter in such way that tip do not create destructive impact to the material (it also depends on the probe’s stiffness). Feedback system maintains the constant value of SetPoint < DFL ("Deflection parameter" DFL corresponds to the measured force). Measurement results in the two-dimensional map of measured surface “*Parameter(x,y)*”, e.g. if the parameter is height Z , then image shows the $Z(x,y)$, which is dimensional topography in every pixel of image (Figure 6).

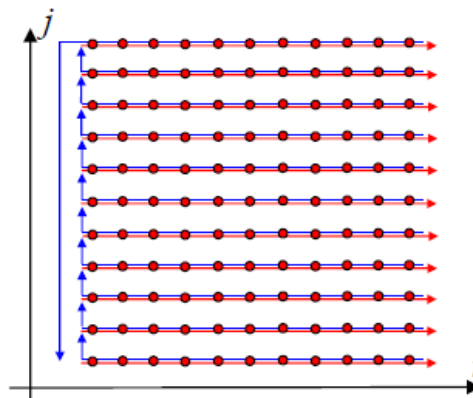


Figure 6. Scheme of scanning process: red is straightway, blue is forward [16]. Data recording is performed in straightway: j is number of pixel line, i is number of position; $i, j = 256 - 1024$.

Relief in AFM can be measured in two possible regimes: Constant force and Constant distance (Figure 7), depending on number of included feedback loops. It should be noted, that the Contact Mode is not applicable for soft and living objects due to the significant forces used. Perhaps it is the basis for precise measurements of solid specimen in metrology.

In the middle of graph of Lennard-Jones Potential (Figures 5, 8 a) it is possible to mark the area of Semicontact Mode measurements. In this mode the probe performs harmonic oscillations and it "rattles" sample’s surface. The impact is less than in Contact mode.

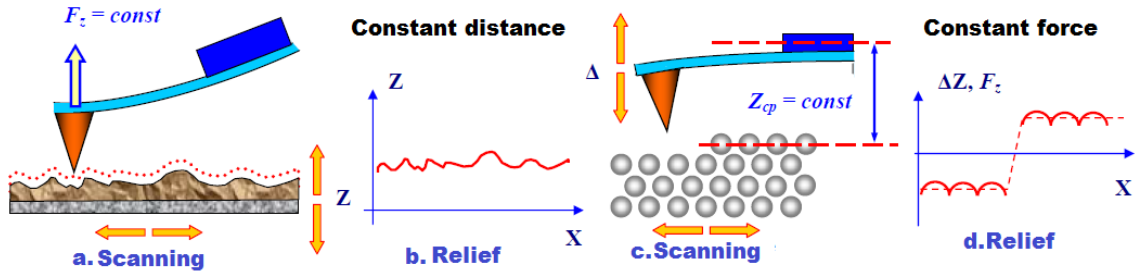


Figure 7. AFM Constant Force (a) and Constant distance (c) modes with topography (b, d) [16].

Initially the probe is vibrating with cantilever's resonant frequency with distance almost 100 nm above the sample without touching it. When vibrating tip is getting closer to the surface, repulsive force is growing and amplitude of oscillations is decreasing, thus feedback system is regulating the specified “SetPoint” value. Feedback commands the scanner to shrink, thus sample is again moving from the tip until amplitude becomes corresponding to SetPoint. One should note that while in Contact mode SetPoint > DFL, in Semicontact mode SetPoint < amplitude (MAG). In such way the middle line of the cantilever trajectory is kept constant, this distance from surface dZ is used as relief. Ideally dZ must be equal to half of Amplitude of oscillations. In this case probe bites the surface in its slowest position and impact is more gentle, even applicable for living cells.

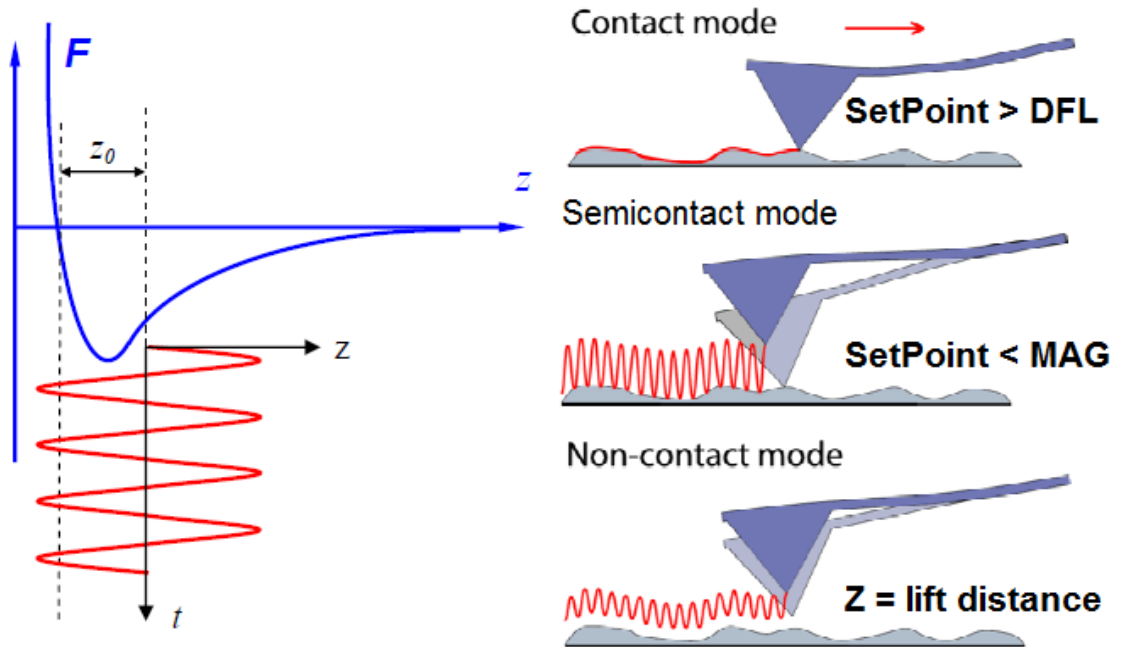


Figure 8. a. Distance in Semicontact mode [16]. b. Principles of three AFM modes [17].

Non contact mode (See Figure 8 b) corresponds to the case when the tip is oscillating with its own resonant frequency f_0 , and it is not touching surface at all. The half-amplitude of

oscillations is less than distance between surface and cantilever's middle line Z_{LIFT} (lift height), i.e. 10 – 100 nm. Usually this mode is not applied at room temperature due to the weak dependence of tip-sample interaction from the distance. However this mode is widely used as a part of “two-pass” technique. In this regime of AFM operation, in first pass (first scanning of the line) the Semicontact topography is measured, and then on the base of the topography the tip goes above the same line with constant specified uplift height Z_{lift} . It seems like the tip returns back to the left side of the image line and tries to show zero topography. In second pass the strong long-range forces can be measured, e.g. electrostatic force in KPFM. The measurement in second pass is more sensitive due to the absence of Van der Waals forces, and also it is more precise due to the z-vertical gradient of measured forces. That is because of the simple assumption that only tip's apex is interacting with point on the surface but not the whole tip cone and rather big cantilever plate. In second pass such forces can be negotiated and force influencing the tip is connected only to the apex, which gives correction to the position of cantilever, found from equation (k_T is cantilever's spring constant) [16]:

$$\Delta z = \frac{dF}{dk_T}$$

Simultaneously phase angle is shifted (Q is Quality factor, i.e. measure of energy losses):

$$\Delta\varphi = \frac{Q}{k_T} \frac{dF}{dz}$$

The phase shift of the cantilever $\Delta\varphi$ is measured by the block unit (in accordance to shift in resonant change of DFL) regarding the exciting electrical signal. Since Quality factor and stiffness are known for cantilever, thereby measuring the phase shift it is possible to calculate the derivative of the force influencing the tip. It is worth noting that the derivative shows sharper change in the force parameters, it can be tracked more accurately, e.g. in Chapter 5 will be compared results for KPFM and KPFGM.

The constituent elements of the AFM

For further detailed discussion of AFM capabilities it is necessary to describe its basic components. One can recall 4 main elements of AFM scheme [16]: 1) probe attached to a flexible cantilever; 2) piezo-scanner used to move the sample relative to the tip; 3) optical detection system (laser and photo detector), providing information of the bending angle of cantilever; 4) feedback system. In addition, it is possible to name few separate additional components: measurement electronic unit, personal computer, vacuum pump, vibration isolation table etc.

The probe. Probe is the starting element of the AFM setup. It is usually a pointed pyramidal needle with tip angle 10 – 20 degrees, fixed on a flexible cantilever unit (Figure 9). Most often tips have slightly elongated shape, but it can be considered as a perfect cone for simplicity. Probes are made of Polysilicon or Si_3N_4 . Dopants cause undesirable increase of apex radius R .

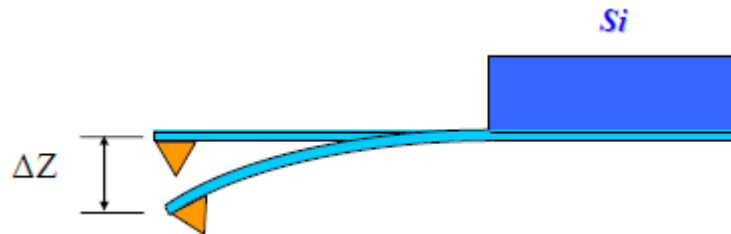


Figure 9. Scheme of the cantilever with tip in forced movement [16].

Three main parameters characterize the tips: 1) tip's apex radius (usually called as tip radius R); 2) cantilever elastic coefficient k_T , and 3) cantilever resonant frequency w .

Tip radius is critical factor for limiting the resolution of AFM scanning, e.g. for 10 nm radius the lateral resolution of topography is limited to few nm. Usually tip radius have rather large value, from $R = 30$ nm for Tungsten coated, to $R = 20$ nm for thin Platinum coated and $R = 2$ nm for Si tips without additional coatings. Coatings increase R (Figure 10), but they provide special features, e.g. ability to measure electrical or magnetic properties. A tip coating seems to be fragile and limits the possible voltage range for electrical measurements by ~ 10 V. If the metal layer will be broken it can cause convolution effects seen in the measured topography.

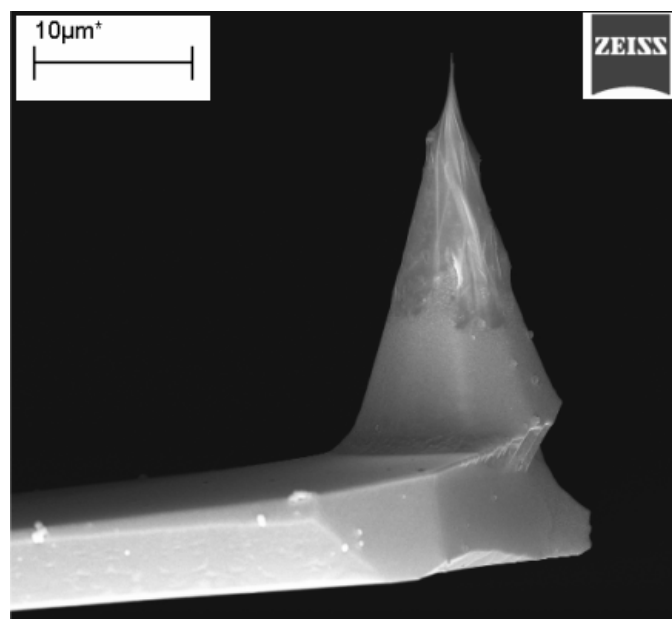


Figure 10. SEM image of NN-T190-HAR5 tips: radius = 50 nm, angle = 12° . [Image courtesy of K-Tek Nanotechnology, NT-MDT, Russia]

Elasticity coefficient of cantilever k_T is in interval 0.001 N/m - 10 N/m [17]. k_T is related to the magnitude of displacement of the tip height ΔZ and force F by equation $dk_T = \frac{dF}{dZ}$.

The smaller k_T , the more suitable probe is for measuring delicate specimen such as living cells (typically 0.01 – 0.03 N/m). Large k values are used in tapping mode, since magnitude of the forces is less to increase the scanning speed. For the correct working conditions, AFM tips should provide the resonant oscillation properties. The resonant frequencies of the cantilever oscillation have bandwidth 10 – 1000 kHz, labeled by manufacturers. Bending frequency is determined by the formula [16]:

$$w = \frac{\lambda}{l^2} \sqrt{\frac{EJ}{\rho S}}$$

where l is the cantilever's length, E is Young modulus, J is a cantilever's moment of inertia, ρ is material density, S is the cross surface area and λ is numerical coefficient for different vibrational modes (Figure 11).

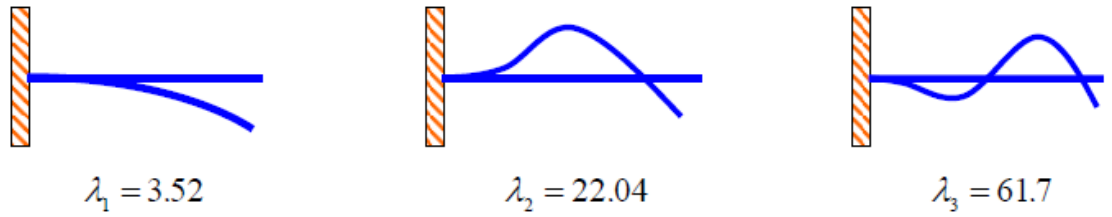


Figure 11. Major mechanical modes of tip's bending vibrations [16].

Quality factor Q is related with resonant frequency f_0 and width "df" of $\text{Mag}(f)$ resonance curve. For vibrating cantilever Q is a measure of energy loss of oscillation, $f_0 \sim 300$ kHz, Q in air is nearly 100 [18, 19]

$$Q = \frac{f_0}{\Delta f}.$$

In UHV conditions Q grows by factor of few hundred, nearly 500. In addition, Q can lead to the explanation of the increasing resolution of gradient mode mentioned earlier. Considering time scale of amplitude change in force mode [18], it is

$$\tau \sim \frac{2Q}{f_0}.$$

However, in phase modulation gradient method

$$\tau \sim \frac{1}{f_0}.$$

Thus time scale τ is nearly 500 times smaller for UHV, which is reason for rise in spatial resolution [19].

The Scanner. Scanner is a device that moves the sample relatively to the AFM probe to perform raster scanning in AFM. Piezo-scanner consists of a radially polarized piezo ceramic tube made usually of PZT material with metal electrodes coating on the four sides (Figure 12) Scanners with constructions of plates and bimorph elements are also possible. Two types of mounting the scanner are used. First is scanning “by sample”, when piezo is attached to a sample holder (used in NTegra Aura device). Sample surface is moving and pattern is measured more accurately, because optical detection system is not moving. Second assembly is scanning performed “by probe tip”, when sample has a fixed position and piezo-scanner is attached to the moving probe.

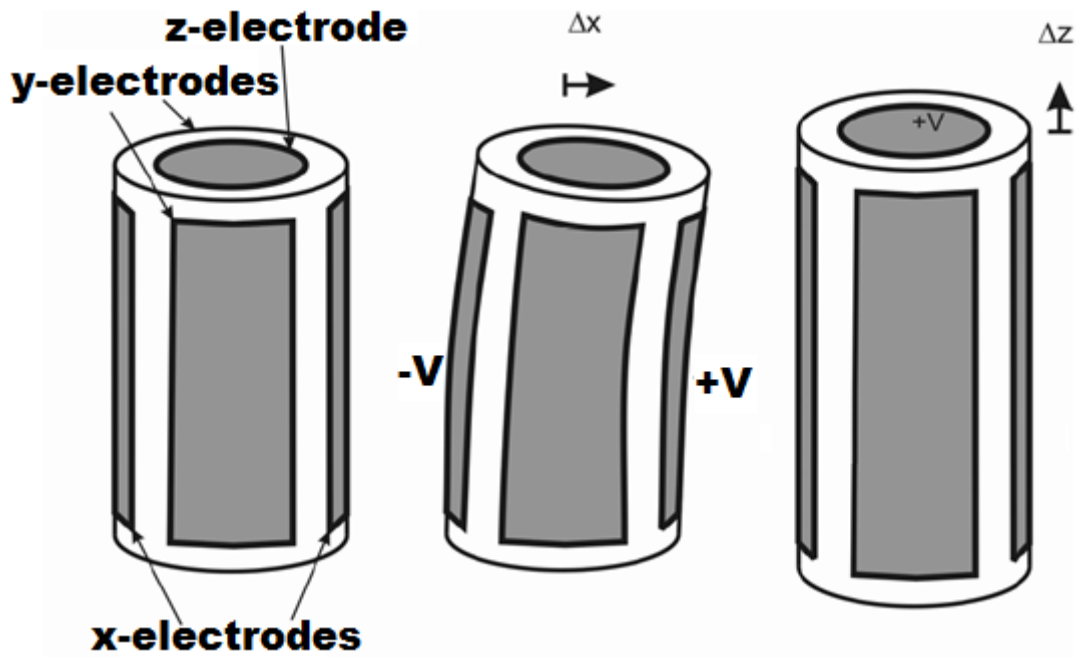


Figure 12. Operational principle of piezo scanner's tube movement.

The piezoelectric effect is used for precise movements of scanner. Piezo ceramic resizes under an applied voltage. The equation of the inverse piezoelectric effect [16]

$$u_{ij} = d_{ijk} \cdot E_k ,$$

where u_{ij} is strain tensor, E_k is electric field component, d_{ijk} are the coefficients of the piezo coefficient's tensor. Tensor of piezoelectric coefficients depends on the properties of piezoelectric ceramics.

When voltage applied to the x-electrodes have different signs, tube is deflected in the x-direction (See Figure 12, central image), same situation for y-electrodes. Thus, probe can be laterally moved along the surface in the x-y dimension. Upon application to the z-electrode

voltage with respect to both x, y-electrodes (See Figure 12, right image) either elongation Δz or shortening of piezo occurs depending on the sign of the voltage. It enables to displace the probe in z-direction normal to the surface.

Thus movement of the probe in three dimensions (x, y, z) is possible for scanning. Scan areas range from few nanometers to several tens of microns depending on scanner and the voltage applied. Piezo-scanner in AFM can move probe relative to the sample in all three directions x, y, z and scan with accuracy nearly 10^{-12} m [20].

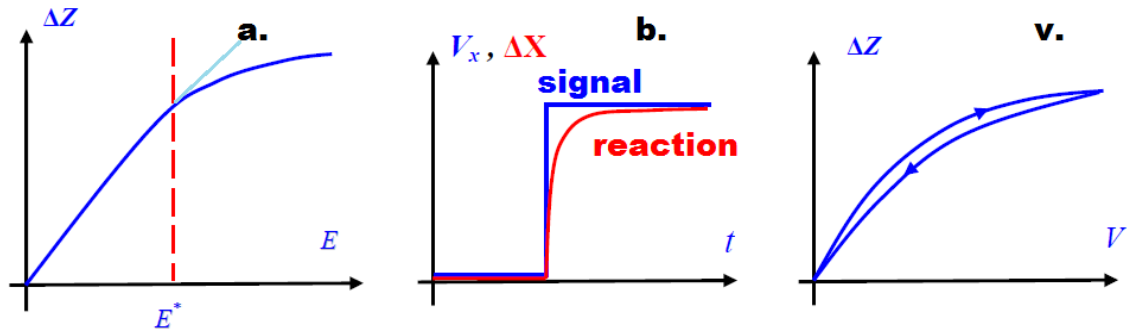


Figure 13. Piezo ceramic disadvantages: **a.** nonlinearity; **b.** creep; **c.** hysteresis [16].

Piezo ceramics have deficiencies [16] which should be considered when measuring and storing the scanner. First of all, nonlinearity of piezoelectric ceramics exists (Figure 13 a). This reveals in deviation from the linear dependence of the change in piezo length with high unit voltage (over 100 V/mm). Second effect is creep (Figure 13 b), which is the delay in response to the controlling field V . This is usually seen in the first scanning point as appearance of a white strip in left side of the frame. That's why first point is usually cropped by imaging software and not visualized. Third, some inaccuracy always exists because of hysteresis properties of piezo ceramic tube to change the length in direction of the electric field (Figure 13 c). This is the reason why measurement is carried at one direction, which is mainly forward (see Figure 6).

Photo detector. Photo detector is the device to measure the deflection caused by the force in the AFM tip in real-time of scanning the surface (Figure 14 a). For this purpose the optical detection system is used. It is measuring the bends of cantilever and consists of: a) 1 mW laser source, which is pointing the beam onto a cantilever and b) 4-sectional photodiode measuring the intensity of laser light reflected from the cantilever to each of its four sections (See Figure 14 b). In order to improve the reflection, a special coating is applied on the back side of the cantilever, e.g. a thin metal film.

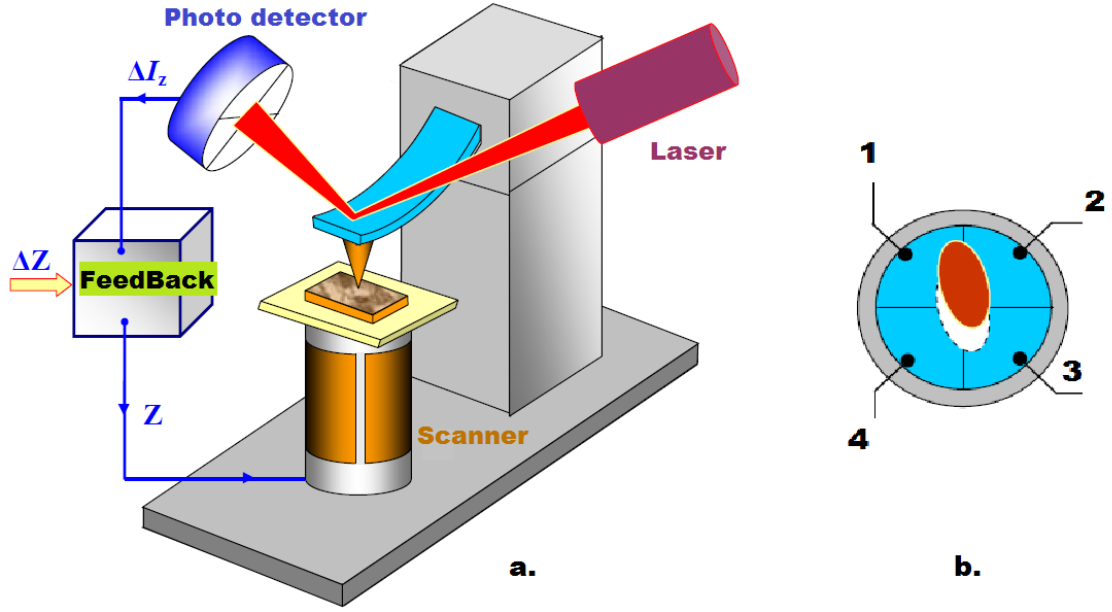


Figure 14. Simplified scheme of the feedback working principle **(a)** and photo detector **(b)** [16].

Before measurements the system is adjusted in such a way that laser beam hit the cantilever and fall into the exact center of 4-cell photo detector. The intensity of light falling on each section should be the same. When additional force F (for example, caused by the interaction of the tip with the surface topography) appears in scanning, this leads to a bending of the cantilever. Cantilever bending causes changing in the angle of the reflected laser beam, thus observed shift of the laser spot at the photo detector appears. The presence of four sections in photodiode permits measuring these small shifts by the difference in photocurrent from different sections. Measurement of the angle of the cantilever deflection (DFL) allows measuring the tip-surface interaction force.

In Figure 14 it is also shown **the feedback system (FB)**. FB performs a regulation function to maintain a constant influence on the probe (in a constant force regime it is F). Minimum resolution of forces in the AFM can be calculated by [19]

$$\delta F = \frac{2kk_BTB}{wQz_{osc}^2},$$

where B is frequency bandwidth and z_{osc}^2 is mean square amplitude of the cantilever vibration.

More specifically, when contact of the probe with roughness causes the cantilever to bend, the position of laser beam on the photo detector changes. Misbalance in the photocurrent ΔI_z is measured as difference in height Z because $DFL \sim I_z$ [16]

$$\Delta I_Z = (\Delta I_1 + \Delta I_2) - (\Delta I_3 + \Delta I_4) .$$

Shift in horizontal axis is measured as $LF \sim I_L$

$$\Delta I_L = (\Delta I_1 + \Delta I_4) - (\Delta I_2 + \Delta I_3) .$$

Measured difference DFL/LF is used by a computer system which responds by compensating voltage to the scanner to minimize the DFL/LF variation. Here should be noted, that nominal force does not matter, it is only important to support the permanent force values.

Accuracy of the scanner positioning is almost 10^{-12} m and laser causes small inaccuracy. Therefore, main scan artifacts appear due to the feedback delay of the scanner. To eliminate artifacts, it is necessary to reduce the speed of scanning. Nevertheless, system performs part of the transformations of constant slope and offset curves. As a result, the measurement appears as checking the value of the measured parameter at a given point (x,y) on the scanned area $Parameter(x,y)$, averaged over the value for surrounding 8 points (Figure 15).

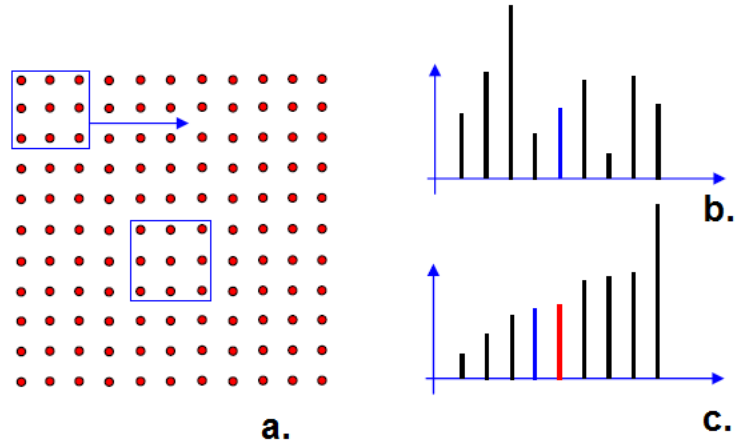


Figure 15. Algorithm of processing the relative measurement by nearest 8 points [16].

a. Measured values; **b.** Distribution by values; **c.** Selection of appropriate value by exclusion.

3.2.1. Electric Force Microscopy (EFM)

Electric Force Microscopy is a “two-pass” technique, which enables to obtain not only the topography, but also the surface potential U , resulting in map $U(x,y)$ [21]. Each line of the AFM frame is scanned twice. Semicontact mode is called the “I pass” and it measures surface topography. In the “II pass” non-contact AFM is performed, probe moves over the surface at a distance of Z_{lift} and repeats the trajectory measured in the “I pass”. Additional voltage

$$U = U_{dc} + U_{ac} \sin(\omega t)$$

is applied between the probe and the surface. Thereby, AFM-probe must be conductive, e.g. it must be coated with a metal layer (usually Pt or Au). The electrostatic interaction energy of the probe with the sample is

$$E = \frac{CU^2}{2},$$

where C is the capacitance between probe and surface. This capacity depends on the z -distance between the probe tip and the surface. Z -component of the electrostatic force acting on the probe is

$$F_z = \frac{dE}{dz} = \frac{dC}{dz} \frac{U^2}{2}.$$

In this case, the derivative is negative for electrostatic attractive force. Since the applied voltage is changing periodically, the interaction force between the probe and the surface will also change periodically

$$F(z, t) = \frac{1}{2} \frac{dC}{dz} (U_{dc} - U(x, y) + U_{ac} \sin(\omega t))^2,$$

where $U(x, y)$ is the local value of surface potential at the certain position (x, y) below the AFM probe. The equation for the force can be divided into three terms, distinguishing the part F_{DC} which is independent of frequency ω , from the first and second harmonics by ω [19]:

$$F_{DC} = \frac{1}{2} \frac{dC}{dz} \left((U_{dc} - U(x, y))^2 + \frac{1}{2} U_{ac}^2 \right),$$

$$F_{\omega} = \frac{dC}{dz} (U_{dc} - U(x, y)) U_{ac} \sin(\omega t),$$

$$F_{2\omega} = -\frac{1}{4} \frac{dC}{dz} U_{ac}^2 \cos(2\omega t).$$

It can be seen that the first harmonic of the electrostatic force F_{ω} depends on the local value of the potential $U(x, y)$ for the AFM probe. Amplitude of the forced oscillation frequency measured in "II pass" for the cantilever at ω is proportional to the magnitude of the first harmonic of the electrostatic force F_{ω} . Since the values of dC/dz , U_{DC} and U_{AC} are recorded in "II pass", the resulting mapping of $F_{\omega}(x, y)$ will contain information only about the distribution of the surface potential $U(x, y)$. Force accuracy in this method is piconewtons. It should be noted

that the measured difference ΔV includes not only the capacity value of the probe and the sample, but also local potential value CPD [19]. This value characterizes the local properties of the surface heterogeneity (influencing the magnitude of the electron work function), and the embedded charge, which will be described for the case of KPFM.

3.2.2. Kelvin Probe Force Microscopy (KPFM)

KPFM is a “two-pass” microscopic study of surface potential [22, 23]. KPFM is similar to the principle of EFM. Topography is measured in "I pass" Semicontact mode. After that, probe is uplifted and in "II pass" the magnitude of electrostatic interaction of sample with an oscillating probe is studied. Thus, topography roughness (Van der Waals interaction) is denied, while tip is used as a reference electrode. KPFM differs from EFM because in "II pass" an additional feedback loop to the voltage U_{DC} is applied, so that F_w vanishes. It is achieved when voltage applied to the probe U_{DC} begins to change and adjusts to the feedback as long as F_w not equals to zero at each scanned point $Z(x,y)$. This occurs if $U_{DC} = U(x,y)$, then values for certain points is recorded by system as local value of $U(x,y)$. Therefore map of the surface potential is obtained. KPFM provides the highest lateral resolution of local potential measurements in comparison to all other techniques: KP, PES, SEM (See Table 2). KPFM was first presented by Nonenmacher in 1991 [24], and method is recommended as unique tool to characterize the electric properties of semiconductor-metal surfaces and semiconductor devices at nanoscale.



Figure 16. Demonstration of **(a)** AFM tip used for KPFM [25] and **(b)** Kelvin Probe [26].

It should be noted that measured local potential difference is equal to the work function of the surface electrons $U(x, y) = V_{CPD} = \frac{\phi_{tip} - \phi_{sample}}{-e}$, where ϕ_{sample} and ϕ_{tip} are work functions of the sample and tip and e is electron charge [19]. With direct contact and applied electrical potential, Fermi levels of both materials are aligned, thus potential of the sample will shift to the level of tip. The external electrical bias nullifies the current, simultaneously the voltage value is defined by system as the local contact potential difference. Therefore this method permits to calculate the sample work function, if the tip's ϕ_{tip} is known.

Concurrently, the information from second harmonic can be further processed by system to get information of the local dielectric constant, local capacity and its high-frequency dispersion.

3.2.3. Force gradient mode in Kelvin Probe Microscopy (KPFGM)

KPFGM is the development of KPFM mode by using the information of the force gradient dF/dz instead of force F for processing data [19, 21-23]. In second pass of KPFGM the phase shift $\Delta\phi$ is measured instead of cantilever oscillation amplitude change. This is why it is also called the KPFM-FM (Frequency Modulation mode), while KPFM is a common Amplitude Modulation (AM) mode KPFM. When measuring the phase shift of the resonance cantilever oscillation, the resolution is considerably higher (Table 3) than that for amplitude measurement (Figure 17).

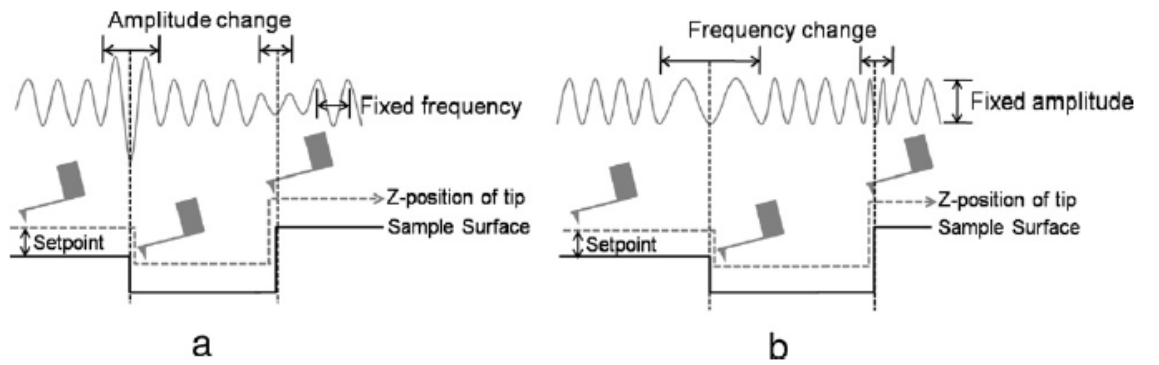


Figure 17. Comparison between Amplitude Modulation **(a)** and Frequency Modulation **(b)** [19].

Mathematical description of KPFGM is discussed in many works as it seems to be perspective technique. The essence of theory becomes clear, if we calculate the derivative of force F :

$$F_{DC} = \frac{1}{2} \frac{dC}{dz} (U_{dc} - U(x, y))^2 ,$$

$$\frac{dF}{dz} = \frac{1}{2} \frac{d^2C}{dz^2} (U_{dc} - U(x, y))^2 ,$$

which corresponds to the phase shift

$$\Delta\varphi(x, y) = \frac{Q}{k} \frac{1}{2} \frac{d^2C}{dz^2} (U_{dc} - U(x, y))^2 .$$

Thus, by measuring the phase angle dependence of $U(x, y)^2$ and finding its minimum, it becomes possible to define $U(x, y)$ with significant accuracy [21, 27]. The accuracy is better because dF/dz substantially decreases the electrostatic interaction of the sample with tip cone and cantilever, which both seem to be considerable, but independent from z , i.e. $d\text{Const}=0$.

Table 2. Comparison of methods of measuring the surface potential [19].

Method	Description	Energy Resolution	Spatial resolution
KPFM	Measuring local CPD of the sample surface	5-20 meV	Better than 10 nm
KP	Measuring CPD of the whole sample surface	1 meV	50 nm [26]
PES	Measuring energy spectroscopy of the whole sample surface	20 meV	Better than 100 nm
SEM	Measuring electron beam induced current to map the surface potential	Not a quantitative method	Better than 70 nm

When comparing -AM and -FM methods of KPFM one should mention that, regardless the lateral resolution of the KPFM-FM is higher, data is usually recorded in degrees of phase shift. This is because KPFGM mapping is based on distortion of the phase fluctuations. In order to get values in mV, special conversion is required.

Table 3. Typical spatial and energy resolution of FM and AM mode KPFM [19].

KPFM mode	Spatial resolution	Energy resolution (meV)
FM	Possibly sub-nanometer resolution depending on tip apex	10-20
AM	Typically 25 nm (sub-nanometer resolution also possible depending on sample)	5

3.3. Nanolithography of charge

Atomic Force Microscope is not only the instrument to study surface, but also a device providing modification of the surface condition in nanometer scale. Firstly, the sharp probe tip can be used in manipulating atoms [28], however for large solid samples it is possible to call another valuable option of AFM - the lithography.

Programmably controlled tip movement can be combined in this technique with applying the impact force, i.e. strong pressure or electrical voltage, to obtain the modified atomic state on the surface during the tip's trajectory drawing. Since the "scanning" regime is operated in non-destructive impact, when system uses the mentioned SetPoint parameter to influence the surface atoms only with elastic force, the "lithography" is different by the enlarged value of "SetPoint" (for mechanical modifying). Second possibility occurs when the external voltage is applied to the tip in accordance to the sample. With charge nanolithography it becomes possible to inject the required amount of electrical charges into the sample (usually dielectric) which could be used to deposit information in bits. Another option is oxidizing the small area of semiconductors in transistor technology.

Two possible regimes of movement can be distinguished in nanolithography. They are separated by the type of used sample image and tip movement consequence. The first algorithm is called Vector lithography. It uses the specified commands of tip trajectories as simple geometrical objects: squares, points, lines, circles etc. High operating speed is the main advantage of Vector lithography. In our work the charging experiments were performed with this type of Nanolithography by using points to inject the charges.

The second algorithm is called Raster lithography, because it uses the raster images to obtain information of the required impact. The tip is moving by the whole image line by line as pixels are measured to obtain value of color intensity. While AFM scanning measurements are providing mapping by desired *Parameter(x,y)*, in Raster lithography the system uses information of every pixel to result its color intensity on the specimen. This type of lithography was tested in our work (See Section 5.3) to obtain microscopic image of LUT logo.

3.4. State-of-the-art systems for SPM

The equipment for surface investigations has been developed, since it has shown prospects for high technology applications. The first topografiner was invented in 1972, which gave the basis for construction of STM [29]. A large variety of other Microscopes was launched by scientific groups, however first prototypes are usually intended to be single-option devices [30]. Nowadays, multifunctional devices have appeared which provide opportunities for comprehensive and precise investigations. Few prominent SPM platforms can be briefly mentioned. Each of them offers appropriate features.

3.4.1. "NT-MDT NTegra AURA" device features

NTegra Aura device is the SPM for studies in the controlled conditions of low vacuum, gases/liquids and external magnetic fields with more than 40 measuring modes included [31]: STM, AFM (contact, semi-contact, non-contact), MFM, EFM, SCM, Kelvin Probe Microscopy, Lithography etc. This allows investigating physical and chemical properties of the specimen with accuracy almost 2 nm. The system permits high frequency regime of operation, which is essential for vibrating oscillations in Semicontact mode. At the same time sensitivity of the synchronous detector is up to 0.01 degree. Scanning system realizes the scanning by sample, scanning by the probe and double scanning modes of operation. Maximal scanning field is limited by 0.2 mm x 0.2 mm x 20 μ m with scanning step nearly 0.001 nm. Device was used in this work. Its main internal components are presented on Figure 18.

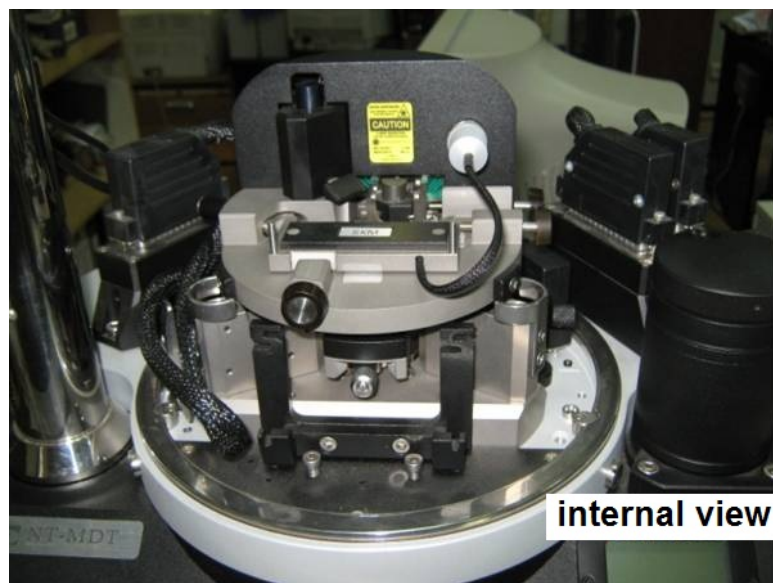


Figure 18. NTegra Aura device without vacuum hood [Image courtesy of PortalNano.ru, Ministry of Education and Science of Russia].

3.4.2. "BRUKER Multimode 8" device features

Multimode 8 device provides opportunity to use a variety of SPM methods with highest resolution and operational speed. It has optional modes to develop the system parameters and possibilities. However, the most commonly used modes are included in basic construction: AFM, STM, PhaseImaging, MFM, KPFM PeakForce, Torsional Resonance mode etc. [32]. This device is operated with the ScanAssyst technology to simplify the operational algorithms for researcher. Some of the modes are proprietary: ScanAssyst, PeakForce KPFM, PeakForce Tuna mode etc. Device provides a larger variety of operating conditions and scanners from 400x400x400 nm to 125x125x5 μm and capable to investigate the mechanical properties of fragile objects, polymers and living cells [33].

3.5. Advances in SPM equipment and techniques

In works [19, 21, 23, 28] are presented calculations of the advantages of the vacuum for AFM scanning. It is explained in view of the increasing of Quality factor of the cantilever's oscillation, because less amount of gas molecules are hitting the tip. Vibrations become easier and their magnitude (MAG) increases. Thus it is possible to decrease the system multiplying parameters which cause additional noise. At the same time, vacuum has a drying effect and water layer covering the sample disappears. It can lead to better interpretation and accuracy of the results, because water layer conceals the adhesion and accelerate the charge leakage.

Few research groups are still considering the properties of the liquid [34 - 36] in their works and they describe the mechanics of the water layer-tip interaction as well as water-sample. They are also studying the properties of ionic liquids [36] on the specimen and the affection of viscous liquids to the results of scanning. These investigations seem necessary to be implemented in living cells investigation due to the fragile structure of the cell membranes (which are also covered by liquid layer). Progress in this study is expected in 2015 (Figure 19).

Distinguishing of the mechanical properties can result in the additional information about the surface adhesion, stiffness and phase [32, 33]. The development of the mathematical basis of such systems has already been used by Multimode 8 device PeakForce QNM mode.

The main claim of the research groups is that tip structure seems to be predominant factor in scanning resolution. Some researchers adhere to the idea of sharp nanometer thin tips, even consisting of one carbon nanotube. However in Binnig and Rohrer works in the 80s, authors

already stated as fact: though monatomic tips are necessary for STM, the shape of AFM tips should be cone-like [37]. The fundamental work on the increasing of the resolution and contrast in KPFM had resulted in the idea of not sharp, but blunt elongated tips [38]. Tips should be accurately calibrated [39], and long durable probes providing high spatial resolution for SPM is predicted until 2015 [40].

Remarkable attention in enhancement of AFM is put to the 2-pass technologies of AFM, or even multitip platforms “Millipede” [40, 41]. This construction allows measuring the surface with increased speed and can be used in Nanolithography for production of precise marks on the coatings to save data. The multiprobe scanning probe microscope (SPM), in which several tips or cantilevers are moved independently, is supposed to be a versatile tool for electrical characterization at nanometer scales [28].

A big amount of works is discussing the developing of chemical bond study, due to the opportunities to detect electrical forces at sub-nanometer range [40, 42]. Here can be noted that some details of chemical interaction and chemical reactions can be studied using the Scanning Probe Microscope platforms.

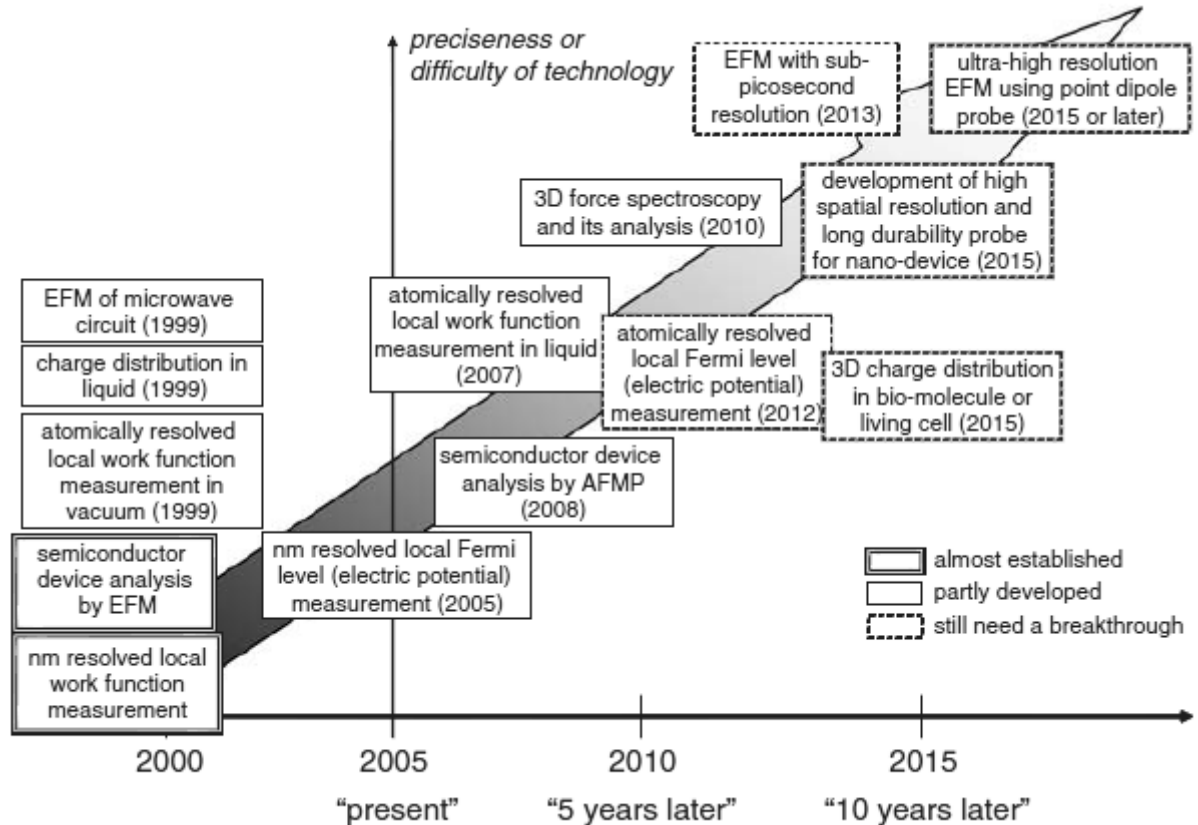


Figure 19. Roadmap of EFM family by 2006 [40].

According to [28] atomic manipulation will become a common procedure in nearest future. The Scanning Probe Microscopy Roadmap 2006 also calls Nanolithography as one of the most probably enhanced techniques in nearest decade [40].

Finally, it is worth saying that development of the data analysis could become as one of probable advantages in SPM, for example in study of the KPFM-FM. Due to the improved resolution of this method it can be used to obtain the map of electrical properties. However, special treatment should be performed to obtain values of potential. Partly this problem had been solved by AFM research group in Ioffe Institute.

3.6. Software for data and image processing

Software is used in Scanning Probe Microscopy at two stages: to process the data (feedback) and to handle the scanned images. Since all algorithms of processing the data have the same mathematical basis, though with details, certain image processing programs are strongly valuable. Many purchasers of SPM platforms have their own appropriatory packages, e.g. in this work is used NT-MDT "*Nova Image Analysis*". "*FemtoScan*" can be supposed also as a multifunctional instrument of analysis, while among the freeware programs can be mentioned "*Gwyddion*" [43], which relies on processing the images for a variety of file formats (it is working in shade tones). Here should be clarified that all images obtained in scanning are made with imitational colors, since SPM is not an optical method [44]. All images in the Results Chapter are presented in the red-black tones.

4. Experimental Part

In this Chapter the methodology of our study is presented with experimental sequence. One can confidently suppose that the experiment is largely dependent on the available information about the samples. Without denying the chemical law of definite proportions, method of growing the sample (regime and conditions), with preliminary visual information about the sample, roughness, reflection, contaminants and fractures, seems highly significant. Frequently the required information is missing. When measurements are carried out for other researchers, often happens that they do not provide important information about their materials for the background. It is a difficult question for Scanning probe microscopy specialists to examine the surfaces properly. If any artifacts, contaminants etc. are even macroscopic (apparent to the naked eye) then results of the experiment can be distorted. This is associated with high locality of SPM measurements (now as a drawback of SPM): if the measurements are performed on the defect or contamination area, then will be monitored exactly the properties of these imperfections (instead of the sample material properties).

When formulating a task, operator of SPM device should consider the existing information about the sample and abilities of microscope, i.e. the Modes. The definite impact to the sample gives reaction in real-time and examiner relies on personal experimental sense. However, critical mistakes can be prevented by an approximate first probe experiment. General basics presented below, including system parameters (MAG, DFL, amplification, lift height dZ , Voltage etc.) and sequence of handling the images, can be assumed as universal for future investigations.

4.1. LaLuO₃ thin films

Two samples of high-k dielectric lanthanum lutetium oxide were objects of our investigation. Samples were obtained from the Laboratory of Research Center Julich (Germany) and they looked like dark squares nearly 1 cm² each. The first sample (it is further called "**Sample #6**" due to its catalogue name) consisted of Si wafer covered with 6 nm thick LaLuO₃ coating made by MBE technique in room temperature. Due to the observed features (defects) of its morphology, little attention might be paid on the basics of this method.

Molecular beam epitaxy is a technology based on the evaporation of material to the crystal substrate wafer, applied in extra high vacuum conditions. It can be used for growing the heterostructures and thin films, however MBE is exigent and rather slow method with growth

rate nearly 1000 nm/hour. Vacuum required for this technique is 10^{-8} Pa, the cleanness of the materials must be at least 99.999999 %. Material is evaporated in heated tigel and then transferred by the molecular source to the heated wafer [45]. The basic scheme of MBE operation is presented in Figure 20.

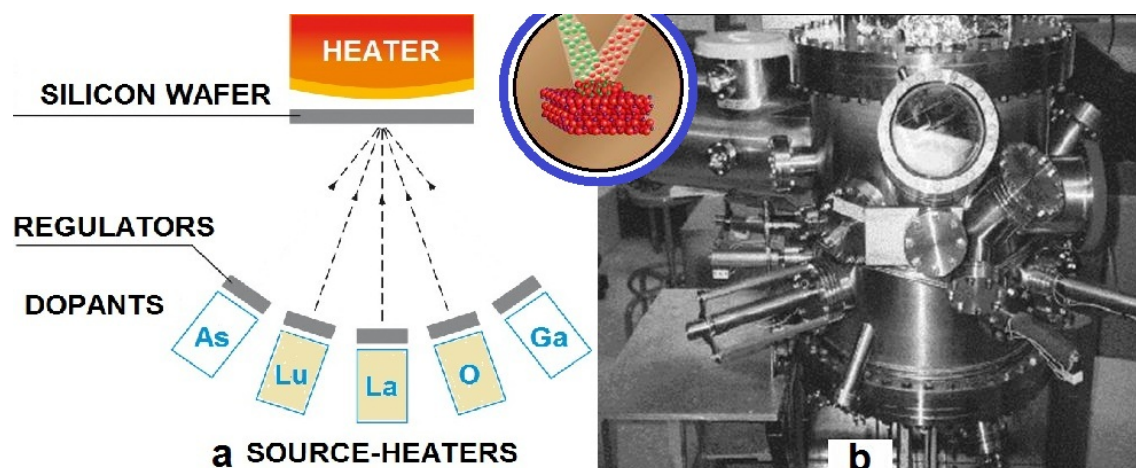


Figure 20. Experimental facility scheme (a) and device (b) used for MBE. [Adopted from Image courtesy of Gusev A.I., Academic, Russia]

To prevent confusion in the further presented Results, must be separately noted that **Sample #6** was divided in two parts before the temperature measurements to avoid overheat. The exact part of the sample used for further investigations was called "**Sample 6.2**". Results for its comparing investigations are presented on the Figure 38 and in Section 5.2.4. The own potential of this sample was measured to be nearly -0.8 V – -0.6 V and partly it was attributed to the noise of working Thermal Module. Nevertheless, the potential difference between own and applied potential values was considered in further calculations.

Note that Sample 6.2 was originally a part of Sample #6, thereby they were expected to exhibit same properties, however the measured properties were different. It is assumed to be caused by structural nonuniformity of Sample #6. Only two coatings were investigated in this work.

The second sample (it is called "**Sample #7**") consisted of Si wafer with 25 nm film of LaLuO_3 , made by the Pulsed Laser Deposition (PLD) technique with additional heating 450°C. PLD is a preparation of coatings by condensation to the substrate surface of the products of reaction between the target and with impulse laser beam with power nearly 10^8 W/cm².

These methods are widely used in production of thin layers (See Table 4), each of them have advantages and weaknesses. For our study only the quality of the surface is meaningful, and it should be pointed out that MBE is considered to show excellent surface quality.

Table 4. Thin film deposition technique comparison chart [46].

	ALD	CVD	Sputtering	PLD	MBE
Thickness uniformity	Good	Good	Good	Fair	Fair
Film epitaxy	Fair	Poor	Poor	Good	Good
Stoichiometric uniformity	Good	Good	Fair	Good	Good
Number of materials	Fair	Fair	Good	Good	Fair
Low-temp deposition	Good	Poor	Good	Fair	Fair
Production yield	Good	Good	Fair	Fair	Poor

4.2. Sequence of the measurement

In this sequence is presented basic operational principles of Scanning Probe Microscope NT-MDT NTegra Aura. The device allows measurement and operating of the data with *Nova* software package.

Presetting. Preliminary, all the facilities should be turned ON and warm up for few minutes.

1) The probe installation. Operating with the Scanning probe microscope is done not only by the computer and SPM device, but also by the hands. Since probe installation is a delicate procedure and it is performed manually, it is needed to follow the regular algorithm. Firstly, the probe is taken from its box with adhesive coating on the bottom. It should be lifted by the short side (probe is rectangular) with the help of tweezers. At this time, the small dots on the long sides can be found by eyes though with difficulty. It is the cantilevers itself, with length of nearly 150 μm and width 35 μm . Sizes can be noted descendingly: probe [5 mm] - cantilever [35 μm] - tip [5 μm] - tip's apex [20 nm]. The cantilever is recognizable only with optical microscope and tip's apex is touching the surface, to observe its shape an electronic microscope is needed.

The sample of investigation is placed on the polymer plate (made of polycor protective compound) and fixed. This plate is put on the scanner carefully, without applying too much force on the fragile piezotube. Then the sample surface is electrically grounded to the Earth. The measuring Head with probe holder should be placed above the sample in distance of 3 mm with the help of Head's screws. Otherwise tip can touch the sample and become rendered unusable.

2) Setting the probe. Using the *Nova* software, in AIMING option the maximum value for laser intensity on the photo detector should be obtained. Thus it is needed to turn the screws of probe holder and the resulting red spot (cursor) should be situated nearly at the center of AIMING window (See Figure 21: here DFL is below zero, LF is above zero). Close to zero values for DFL and LF parameters would be desired. Changes of these parameters will be used further by feedback system. After that, the laser spot should be placed right to the center of screen by manually rotating the photo detector's screws. Values of system intensity LASER for platinum tips "fpN11Pt" and the *Nova* package are nearly 32 – 36.

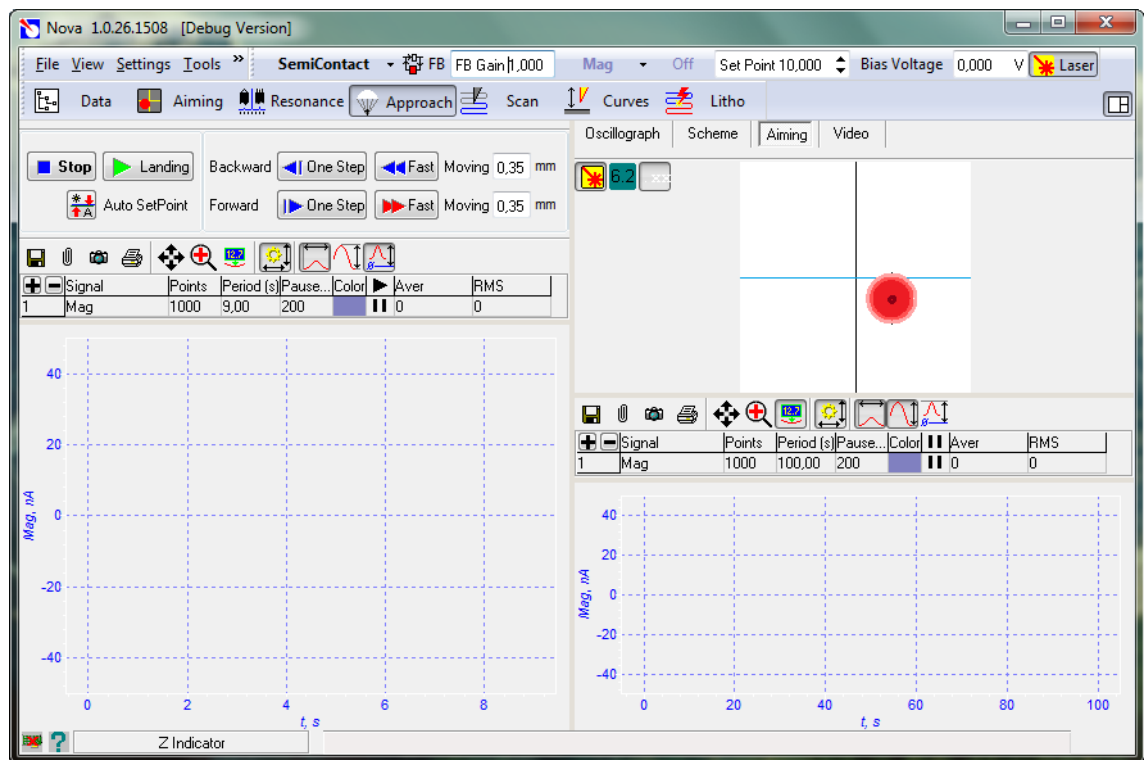


Figure 21. Working window of the *Nova* program. Set regime is Semicontact; used option is APPROACH; chosen parameter SetPoint is 10. Further mentioned options are seen at the left up: DATA, AIMING, RESONANCE, APPROACH, SCAN, CURVES, LITHO. The system performs measurements of MAG parameter. The AIMING window is seen at the right.

Finally, in the RESONANCE option it is required to find the resonant frequency for the cantilever, which has the value of 100 – 200 kHz (indicated on the factory box). It depends on the cantilever material stiffness, its length, temperature and individual features.

As it was told before, LASER parameter is the resulting value of light intensity for photo detector. Due to the peculiarities of the reflection from the cantilever surface and the photo detector's positioning in space, the final setting of the probe must be conducted by the system MAG parameter. For this purpose, in the APPROACH option with indicated DFL on the left, two

additional windows can be switched on to be indicated: 1) the AIMING spot and 2) a plot for MAG in time domain (See Figure 21). With the help of photo detector's screws, a maximum value of $MAG \sim 15$ is needed to be obtained.

3) Setting the scanner. At first, the electronic calibrations can be installed in the system by pressing the "Settings" – "Load calibrations". Except from this step, the scanner should be mechanically calibrated. In *Nova* scheme active window the CLOSE LOOP, XY, NL buttons are used for these purposes, followed by pressing the RUN button. On video screen or ocular of the optical microscope there can be noticed movement of sample in respect to the cantilever and its shadow. These calibrations are overwhelmingly important due to the nonlinear mechanical properties of the piezo ceramic tube. The tube can stagnate with time and thus creep effect will result in the image's artifacts (see below). Finally, the buttons NL, XY, CLOSE LOOP should be pressed again, in reversed order.

4) Creating the vacuum conditions. The safety hood should be put upside measuring Head and sample. In NTegra Aura device, it is possible to protect the sample and measuring system from acoustic noise and to obtain the depressurized atmosphere (this feature is missing in BRUKER Multimode 8 basic configuration). In enhanced devices, the hood can decrease the affect of electromagnetic noises and undesirable optical radiation. After the pump is switched ON, the safety hood is plugged into the vacuum pipe.

Vacuum is used for many reasons, e.g. it creates the reproducible atmosphere, and it minimizes the affection of dust particles (and gas molecules) to the cantilever and tip. This increase the Quality factor Q . However, the most important effect of pumping is the drying effect. The fact is that atmosphere air contains water molecules as moisture. Therefore, in reality all the surfaces are covered by a water layer of few nanometers thickness. It can affect the measuring regime of the AFM topography and also be the reason of charge dissipation. In reduced atmosphere the surface tension of water is lowered down dramatically and thickness of the aqueous water layer decreases. It is required to apply the additional heating up to 350°C to dry the surface completely, but it is apparent that sample and device are not suitable for such heating. Residual water layer in our measurements is chemically adsorbed on the dielectric surface and its thickness has a value of nearly 3 nm.

It must be noted that the resonant frequency parameter for cantilever f_0 is changing in time because of pumping. Frequency peak becomes narrow (Quality factor Q grows up) and shifts to the left by few hundred Hertz. Simultaneously measured **MAG** parameter is growing up to nearly 50 and it should be decreased by system amplification settings. Pumping lasts nearly

one hour until 10^{-5} bar and during this time it seems reasonable to set up the mentioned parameters of scanner and probe and then check feedback for further measurements.

5) Setting the feedback. In the Semicontact Mode (it is used to protect surface from scrapping for the first measurement, because it affects the surface less than Contact) the **SetPoint** $\approx 0.6 \cdot \mathbf{MAG}$ should be specified. In the APPROACH option, the LANDING button should be pressed. By this action, the oscillating probe tip will come close to the surface and in few seconds the defined system parameter MAG will become equal to **SetPoint**. This is the demonstration of negative feedback, when system reaction is keeping the **MAG** parameter constant in time. Thus the tip-surface influence is the same in all the measured areas of the sample. Scanning in Semicontact mode is performed as the tip is oscillating with frequency nearly 200 kHz, while cantilever is tracking the surface under the set distance (if lower **SetPoint**, then the position under the sample is lower). One should keep in mind that distance between cantilever and sample is not measured as numerical values, as well as the absolute value of **MAG** is not necessary to know. It is enough that these parameters are constant.

6) Scanning in Semicontact Mode AFM. In the SCAN option “Frequency” parameter should be set to 0.7 – 1 and chosen scan size to 10 micron, then press RUN button. It will take approximately 5 min to finish one scanning image of that size. Further it is necessary to process the topography results (See Section 5.1) and make decision about new scanning zone in case of any found defects or asperities. One should remember that higher scanning rates, varied by number of points and “Frequency” parameter, can lead to linear artifacts (See Figure 22, compare with results on Figure 28 b). At the same time, charges in our study are supposed to be dynamic systems, thus it is needed to find optimum speed of scanning.

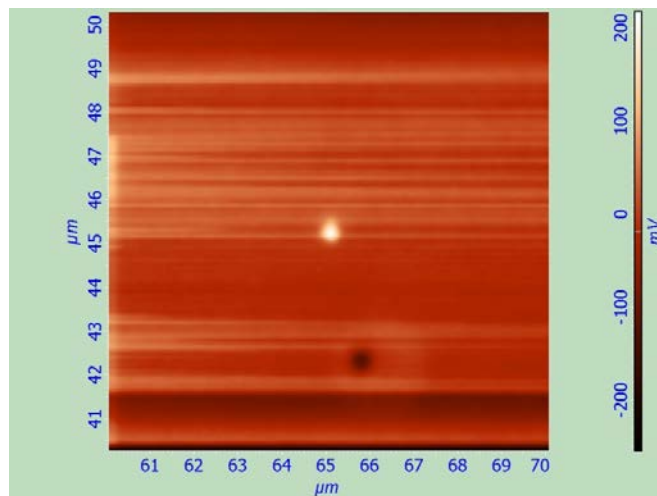


Figure 22. The raw image obtained for Surface Potential. It needs to be fitted.

7) Setting the Kelvin probe Mode. At first, the Kelvin probe Mode should be turned on from Semicontact. Then operate the procedure of checking:

- Open the “II pass” regime by the button of the same name.
- Watch the **MAG*SIN** curve (this signal is proportional to electrostatic force F_w) on the oscillograph in the right and turn off the feedback.
- If **MAG*SIN** is on its maximum, then decrease the **Lock-in Gain**: then use “Amplitude” of electrical stimulation nearly 0.2 – 0.5. By changing the phase of the generator, check that **MAG*SIN** is crossing the horizontal axis, then set the phase for the maximum absolute value of **|MAG*SIN|**. The sign of **MAG*SIN** should be taken such that if “Bias Voltage” is positive, then **MAG*SIN** is decreasing. Concurrently it is required to monitor the noise level. Finally, check that **SetPoint=0**; “FB Gain” is nearly 0.5 – 1.
- Close the feedback loop, simultaneously check that **MAG*SIN** becomes zero.
- Check the parameters of “II pass”, set SURFACE POTENTIAL to be measured.

8) Scanning in KPFM. a. Check that feedback is closed in “I pass”.

- Measure the amplitude of oscillations in “I pass” to obtain the range for **dZ**.
- Use the option CURVES and set the range to be 20 – 200 nm, then set the position of a measured point by cursor and measure the amplitude (See Figure 26 in Results).
- On the basis of this measurement set up the **dZ** parameter. If the amplitude of oscillation is very small then leave it zero.

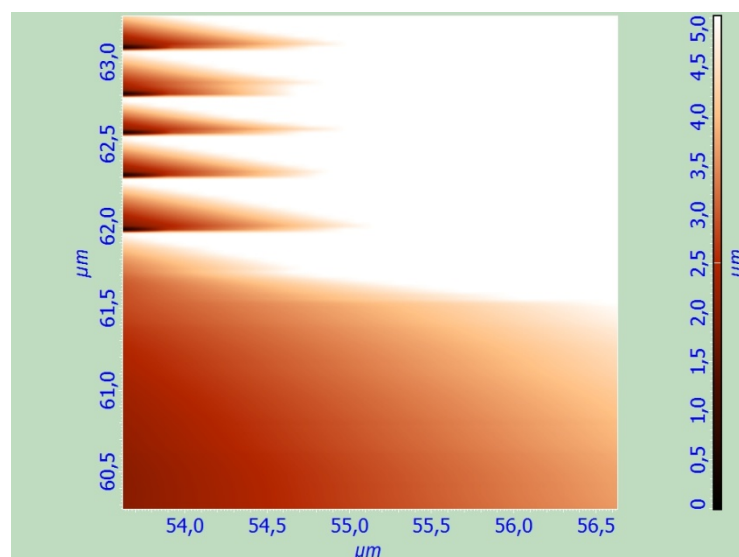


Figure 23. Image revealing artifacts caused by the excess value of lift height.

e. scan the surface by SCAN – RUN. For too high **dZ** the white damaged area will be seen (Figure 23). It is required to decrease the **dZ** parameter due to these artifacts.

9) Charging & Lithography measurements.

In the LITHO option choose Mode “Vector” and Method “Bias Voltage”, then create the new sample. It can be a point or a line. Then it is required to set the Voltage enough for lithography on the basis of chargeability (See Chapters 5.2.1 and 5.2.4). After that, set the Contact mode for scanning (remembering the **SetPoint**), unlock the feedback and set the “Feedback” to **DFL**. **SetPoint** should be changed to be larger than **DFL** signal, and after that close the loop.

Finally, the charging is started by pressing the RUN button. To scan the result, it is needed to set the Semicontact mode, set up the Feedback to **MAG** signal instead of **DFL**. Type in **SetPoint**, which was used before in contact mode, then close the loop. Finally, the scanning is operated by pressing the SCAN – RUN buttons.

10) Handle the obtained images.

Software *Nova Image analysis* can be used for this purpose (Figure 24). Second variant is *Gwyddion* package. *Nova* seems to be more functional for appropriatory NT-MDT file formats.

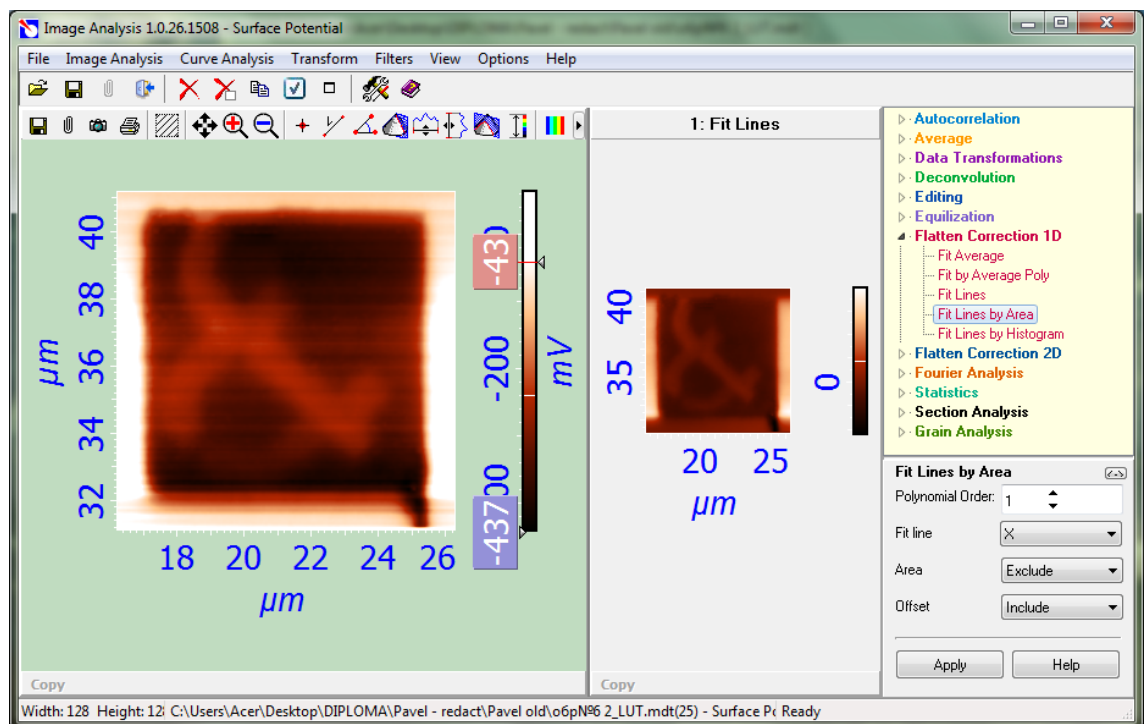


Figure 24. The *Nova Image Analysis* main window, with settings on the right.

In the DATA option of *Nova*, press “Analysis” button on the right. Few operations as “Subtract plane” are usually needed. To remove the feedback delay effects (artifacts), “Select Region” option can be used: “Select region” – “Flatten correction 1D” – “Fit lines by area” – “Fit lines by X” Exclude the area selected. To reduce the noise level, “Fourier Analysis” can be operated. In the “FTT filtering” option it is needed to choose peaks except the central one.

As final result, the fitted and organized image is obtained. Therefore, it becomes possible to measure potential, lateral size and other characteristics of the injected charge. Due to the varying names of the settings and wide opportunities of the image processing software, they seem to be out of range of this Master's Thesis.

Few artifacts can be named to be avoided in measurements. They appear due to:

1. Incorrect cantilever selection. For example, for living cells only those who have spring constant 0.01 N/m should be selected. Some cantilevers have much larger stiffness, 5 – 10 N/m. By using such cantilevers to the soft objects, their surface would be destroyed in Contact Mode. The information about softness is always mentioned by manufacturer.
2. Exceeded value of scan rate. When there is a small disturbance in the analyzed topography, i.e. a hill, then tip position will be higher than the surface for some moment of time, however cantilever is still moving. This can lead to the stretched lines after the roughness found in Semicontact topography. At the same time tip is always returning to the start position on the scan image (originally to the left side), thus the artifacts would be seen from the left side. The light area on the Figure 23 does not mean that there is some object on the left of the image, it is surely an artifact (Compare Figure 22 with the handled image on Figure 4b).
3. Incorrect lift height **dZ**. In KPFM when applying high values of **dZ**, drive amplitude would be larger than possible for measurement of Surface potential. It is seen how tip slips upwards from the sample because of the imperfections in the scanned surface (Figure 23).

The mentioned artifacts can be reduced by proper operation conditions. Thus the system parameters, procedures and settings shown above seem to be valuable for practice. However, some operations are called in different way in other systems and few items (calibration and landing) can be done automatically in more advanced devices. Nonetheless, the experience and skills are required for proper operation of the SPM. The results of measurements of LaLuO₃ presented below are obtained with the help of the methodology described above.

5. Results

5.1. Topography

The topography measurements demonstrated smooth surface (Figure 25) with 2 nm noise [8].

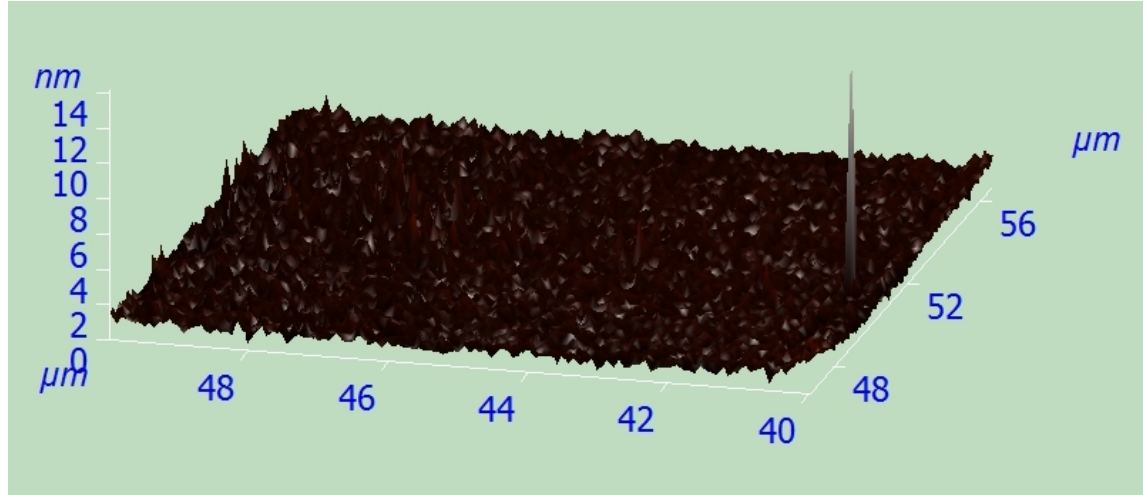


Figure 25. The 3D-recovery of surface topography for sample #6 with artifact on the right.

Few found artifacts did not affect the results of our experiments, at least for the future study only the homogenously smooth surfaces were taken into account. To improve the resolution of scans it was needed to find proper value of height, i.e. the Driving distance between the tip and the sample in Semicontact mode, which was carried out by applying the proper "MAG" system parameter nearly 2.0 – 3.0 [nA].



Figure 26. Mag(z) curve to define the Driving distance value in Semicontact Mode.

For correct measurements, the graph for Mag(z) (Figure 26) should be obtained straight (irregularity due to the Young's modulus is seen) and its slope multiplied by the "Mag" provide nearly 80 nm amplitude for Semicontact.

5.2. Electrical charge behavior

Charging experiment includes two stages: 1) Charging of the point by Nanolithography ("LITHO" in Nova software) and 2) Measurement of the Surface Potential. As a result, the topography scanning is operated in AFM Semicontact mode, the Surface Potential mapping is made in second pass by KPFM. To check the ability of the samples for charging, the probe measurement is needed. Thus, the probe potential +1 V (providing the potential difference of nearly 1 Volt to the surface local potential) was applied for 10 seconds by the small sized tip's apex (approximately $R = 20$ nm for probes with Pt coating). To process the charge behavior measurements it is necessary to define the real time on the scanned position (on the line of the image). If the scan time length is 3 min 10 sec, but the desired spot is placed in the center of the scan, then one can take the time for the charged point: $5 \text{ sec} + 310/2 \text{ sec} = 160 \text{ sec}$ (rather than zero or 310 sec). 5 seconds is the operational time for manual setting of the "Surface Potential" mode from the "Nanolithography" (contact) mode used for charging. After defining the existence of charged spot, +3 V 10 sec charging was used for control experiment (See Figure 28b). The AFM results show clean smooth surface, while there is a charged spot on KPFM. By automated measurement technique for the same position on the sample it is possible to preliminary track the peak potential drop and evaluate lateral size and relaxation time with non-destructive impact to a surface. To find the possible destructive potential difference, the limiting potential experiment was arranged afterwards.

5.2.1. Electrical chargeability

The chargeability can be described as the value of surface response potential U in mV to the voltage V applied to the tip, dU/dV .

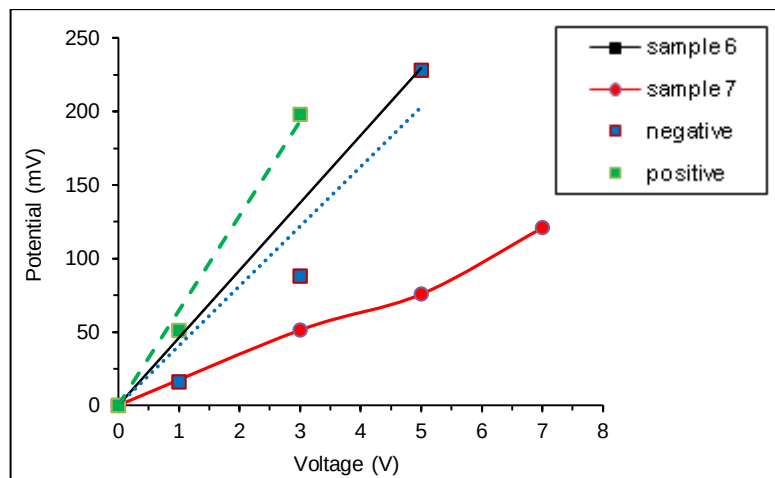


Figure 27. Electrical chargeability of Samples #6 and #7. Note the green squares for positive and blue squares for negative charging for Sample #6. Black curve is for their absolute values.

The chargeability of samples #6 and #7 (as linear slopes for red and black curves) differs nearly in three times, which can be seen in the Figure 27. It is easier to inject the charge into the Sample #6. Data is suggested to be given for same moment, however blue dots show slightly lowered values due to the time difference. But the main reason for observed difference for these charge injections will be discussed later. Here are given maximum values, obtained in experiments with no losses occurring due to the surface defects or electrical system noises.

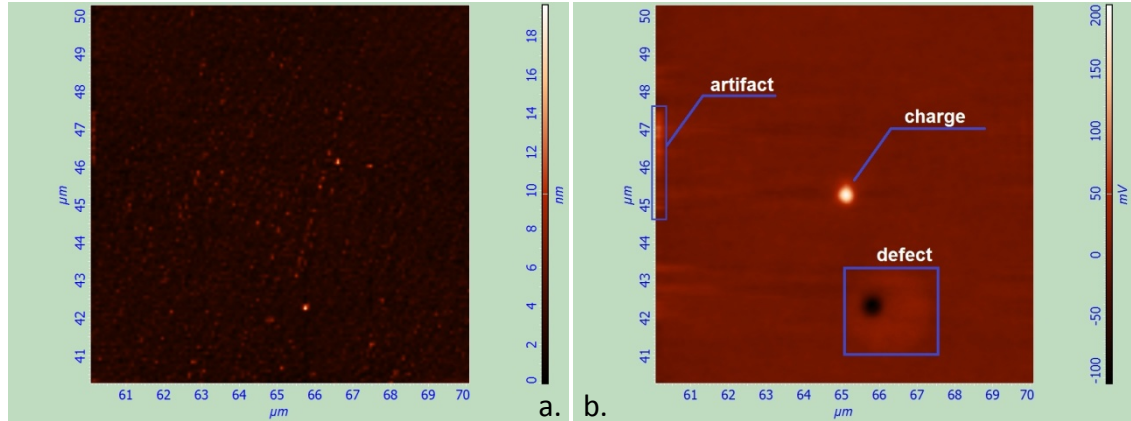


Figure 28. KPFM results for Sample #6 after charging [+3 V, 10 sec]. **a)** AFM surface scan 10x10 μm^2 is smooth; **b)** Surface Potential Mapping reveals charge in the center, FWHM = 365 nm.

Time for the observed drop potential is more than 1 h for Sample #6 and 0.3 h for Sample #7. Peak is decreasing slightly and it has the bell shape, or so called "Gaussian" form (See Fig. 41).

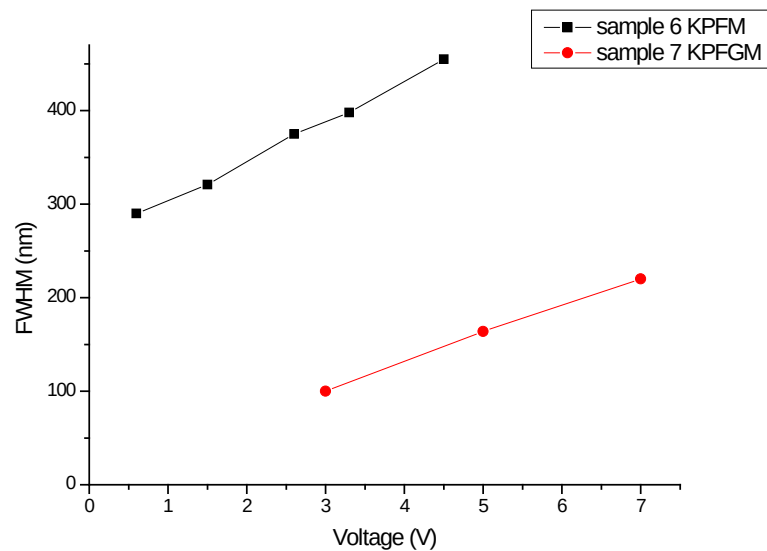


Figure 29. FWHM vs. Voltage dependence for Sample #6 (KPFM) and Sample #7 (KPFM). Coordinate of expected intersection of the FWHM axis denotes operational limit for lateral size in KPFM modes.

The full width at half maximum (FWHM) parameter is not changing in time in our experiment. FWHM for Sample #6 is 365 nm [+3 V, 10 sec] (Figure 28b), while for Sample #7 it is estimated as 360 nm. Thus the FWHM do not depend on the sample. Using the 20 nm thin Platinum tips FWHM = 300 nm was achieved for Sample #7 (*not presented here*), however by using KPFGM method lateral resolution is better than 100 nm in same conditions (Figure 29) [19, 27].

Though, the FWHM parameter strongly depends on the applied voltage. According to the Figure 29, it is possible to track the linear approximation to the potential axis to find the value for the maximum lateral resolution, about 250 nm for KPFGM and 25 nm for KPFGM. Thus, the KPFGM mode is preferable for the measurements because of better resolution, however it cannot provide the numerical values of the Surface potential, because it is measured in degrees of phase shift. That's why for our further experiments KPFGM mode was used, tracking the values in mV (results for KPFGM see later).

One must admit that strange shape objects were found in the first measurements of Surface Potential (See Figure 28b). The object can be described as ellipse with length nearly 2 μm , highly negative core and positive cloud area shifted to the core (See Figure 30). The concentration of these objects seemed to be nearly three on the 20 x 20 μm^2 scan image. They were preliminary distinguished as the surface defects, caused by mistakes in MBE method of obtaining, thus the area with ellipses were not further examined.

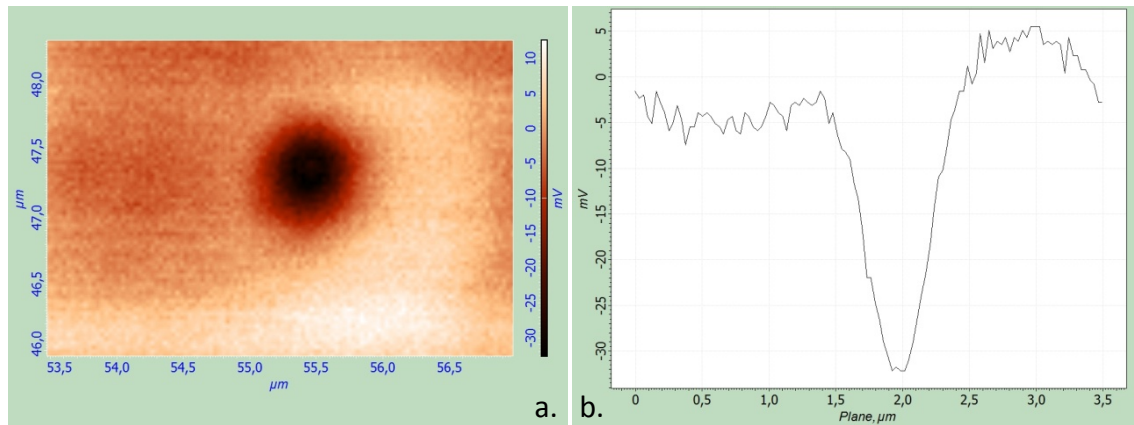


Figure 30. Surface Potential for ellipse shaped defects in Sample #6. **a.** Mapping; **b.** Profile.

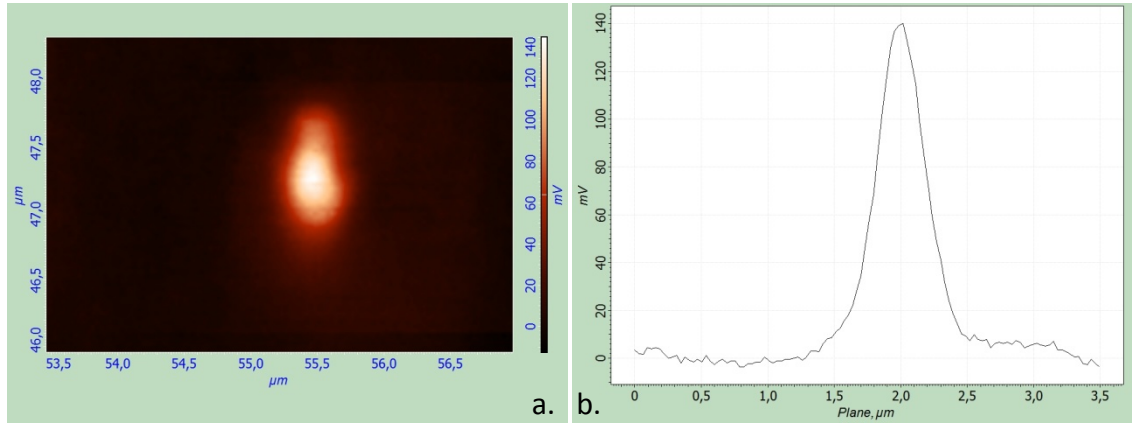


Figure 31. Surface Potential for defects after charging [+3 V, 10 sec]. **a.** Mapping; **b.** Profile.

Such artifacts should be distinguished in order to prevent affecting on the final measurements of charge behavior. Although the ellipses have been perceived for the oddities, reaction to the voltage applied was tested: it was found that average -28 mV core potential (Figure 30) is increased up to the 140 mV (Figure 31), thus the potential difference is nearly 170 mV which is in good agreement with the surface area without defects (compare with Figure 27). Still they were not found in further KPFM scans and didn't affect the results.

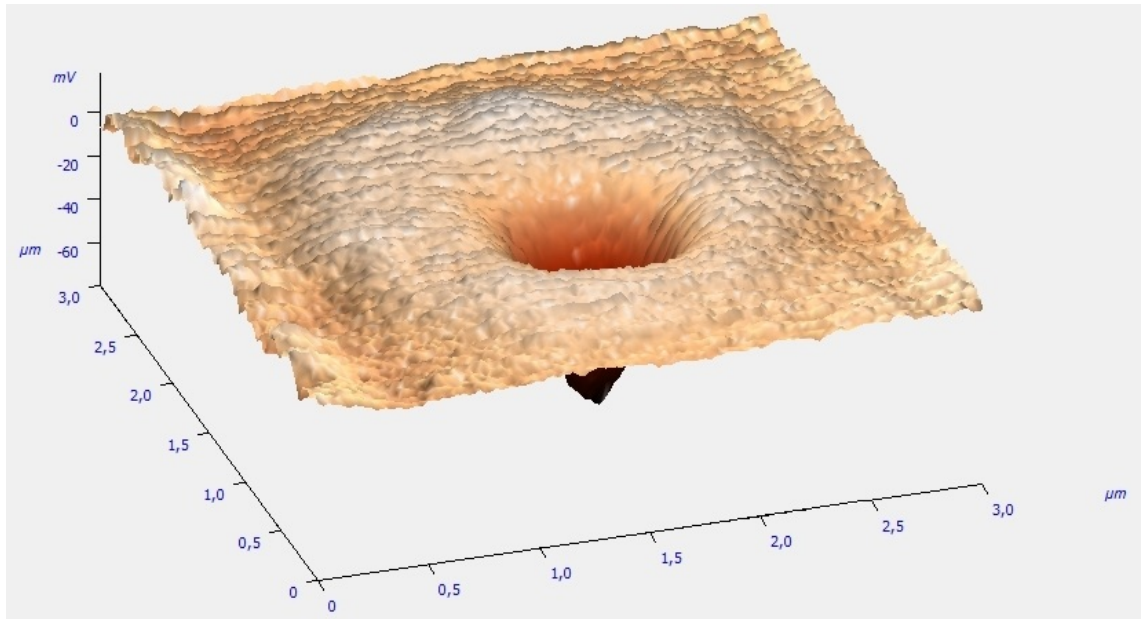


Figure 32. 3D-reconstruction of the surface defect found in KPFM Surface Potential.

One can conclude that samples are uniformly smooth and chargeable: nearly 200 mV and 50 mV for samples #6 and #7 respectively in +3 V 10 sec regime. For more precise description of charge behavior we conducted further research. The artifacts found in Sample #6 (See Figure 32) should be avoided.

5.2.2. Limiting potential of charging

It was necessary to find the range for non destructible voltage that can be applied to the material in our research as well as the limiting potential.

The series of charges was injected to LaLuO₃ film at the distance of 1 μm . The charging time of 10 sec was identical for all five charging voltages: -5V, -3V, -1V, +1V, +3V. Then we used the KPFM for mapping of the charges (Figure 33). The difference in time of the measurement for certain spot must be accounted at the same time as local potential of the surface itself (nearly -0.02 V). However, one can suggest the difference in the charge properties, depending on the charge sign (further discussion of the effect of polarity is given later).

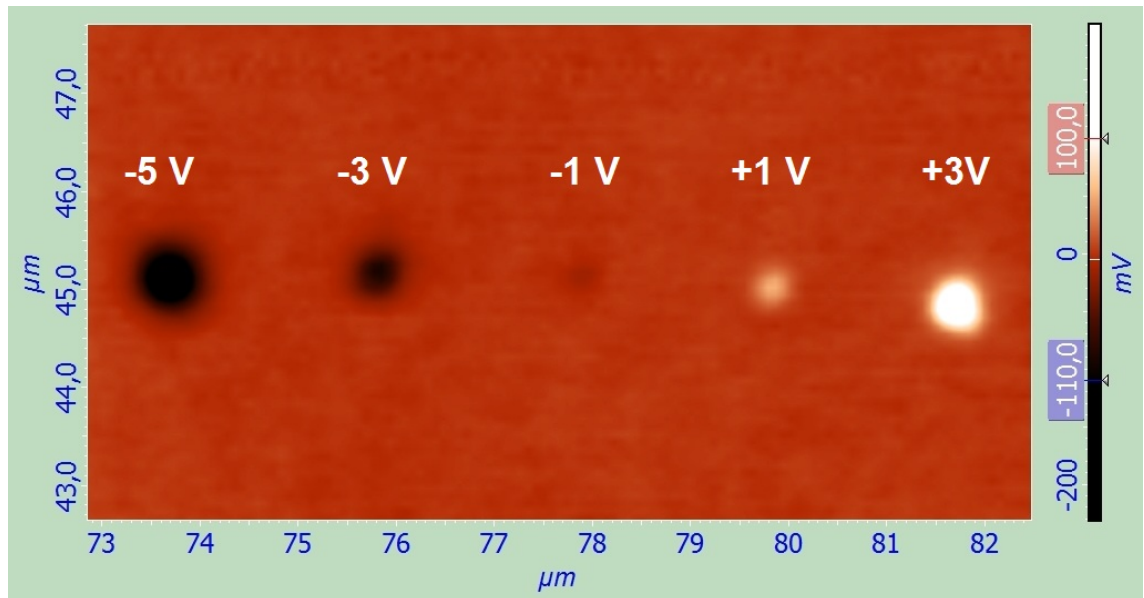


Figure 33. Surface Potential image of a charged series for Sample #6, charging duration 10 sec.

Comparable results for peak height of the potential profile for +3 V 10 sec charging (180 mV, nearly the same as in our previous experiment) was found. Potential curves were decreasing slightly and FWHM was constant in time domain as in the previous experiment.

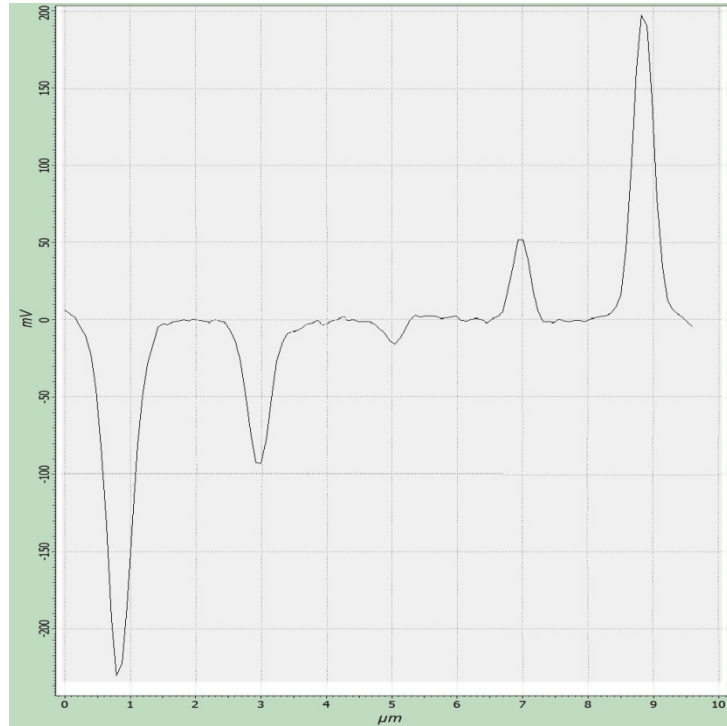


Figure 34. Surface Potential profile for the series of charges.

For sample #6 there are no observed limiting potential according to Figure 33 and potential profiles shown in the Figure 34. The Sample #7 does not demonstrate the existence of critical potential difference such as the Sample #6, at even wider range of $-7\text{ V} - +7\text{ V}$. We preferred to use the $+3\text{ V}$ 10 sec charging regime for ability to compare effects of temperature and time. Critical Voltage for tips was nearly 10 V , thereby it was necessary not to go over this limit.

5.2.3. Induced charge relaxation time

Charge cannot be located within the dielectric layer for the unlimited period of time after injection. This is observed when potential value U decreases. Relaxation time is the time length, when the peak value of potential drops in $e = 2.718$ times. It is supposed to be one of the main parameters of charge behavior, thus it is needed to define precisely the certain potential values and real times of the measurements by algorithm described in Section 5.2.

The series of 3 points was injected in the Sample #6 to find the dependence of potential with time $\text{Pot}(t)$ for different charging duration: 1 sec, 10 sec, 30 sec (See Figure 35).

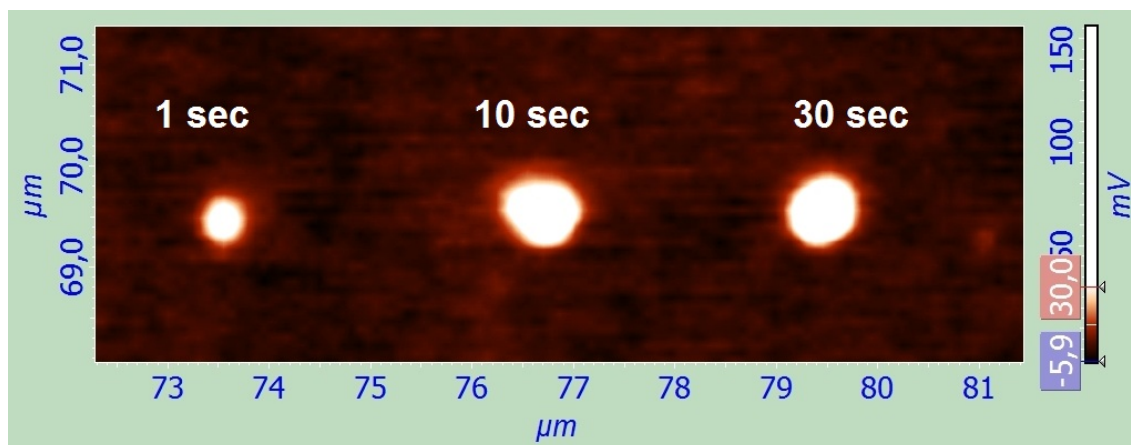


Figure 35. Surface Potential image of a charged series by duration. Charging voltage +3 V.

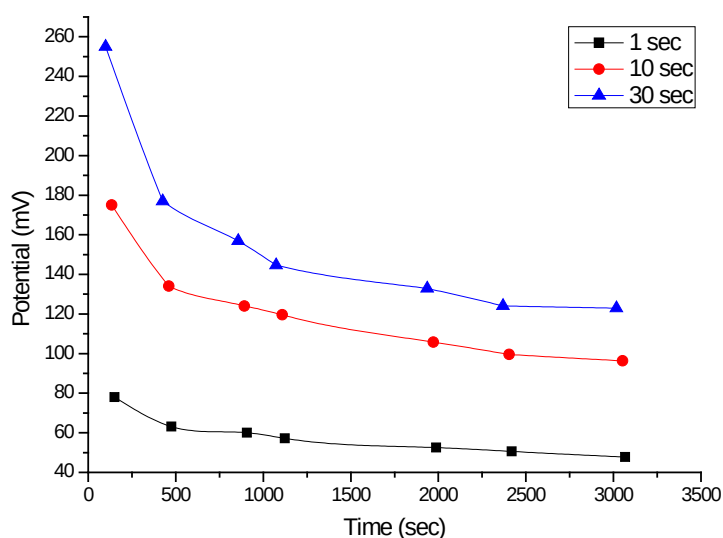


Figure 36. Potential height Pot(t) dependence for different charging duration for Sample #6.

The results for three charging times are shown in Figure 36. It is seen that charging time reflects on the height of potential curve. Also it affects its shape, Gaussian becomes thicker. FWHM and spot lateral size L become wider with increasing the duration of charging. The relaxation time is more than one hour (not measured exactly in this experiment). It should be mentioned here that after the experiments with charging on Sample #6, the measuring system NTegra Aura was devacuumized. After 3 hours of reaction with ambient atmospheric air (moisture and water film should be remembered), the charge spots were still visible (See Figure 37). According to the potential height at start 198 mV, the result after 3 h was 58 mV, i.e. fallen by 3.4 times, while FWHM increased only by nearly 30 nm.

Thus, Sample #6 shows high sustainability to the ambient conditions and remarkable relaxation time of nearly 2 hours.

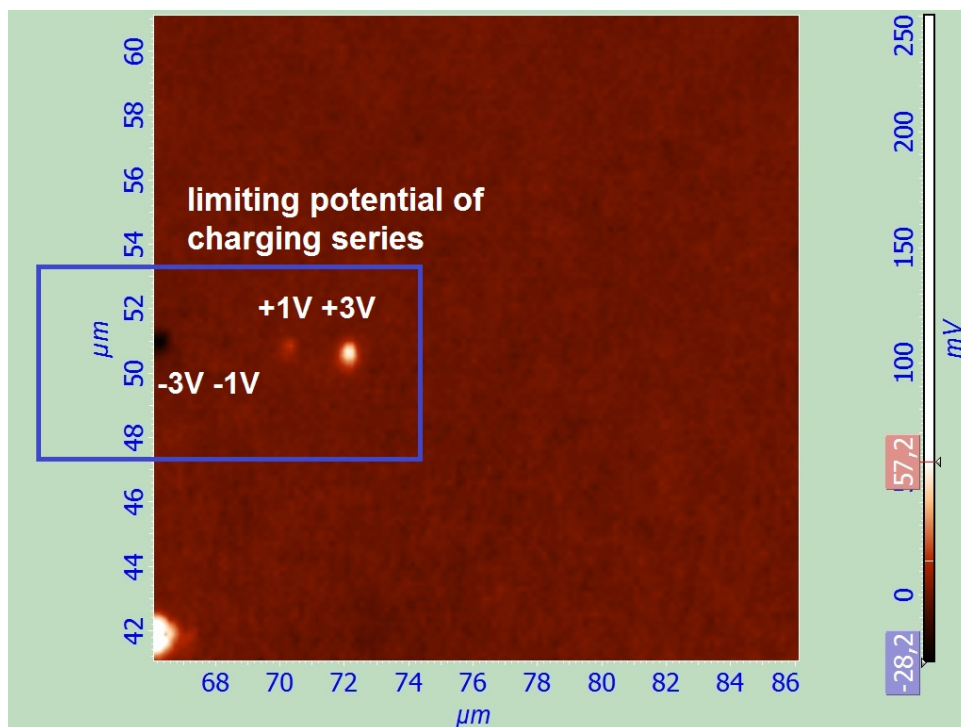


Figure 37. KPFM Surface Potential image of area after 3 hours on atmosphere (marked blue).

For the Sample #7 was carried out similar experiment with longer charging lengths: 10 sec, 30 sec, 90 sec. Relaxation time values were smaller, nearly 0.3 h. However, size of the spots was nearly constant (FWHM ~ 360 nm) for all three injected charged spots and didn't depend on the charging length. Further investigation should be carried out on this issue.

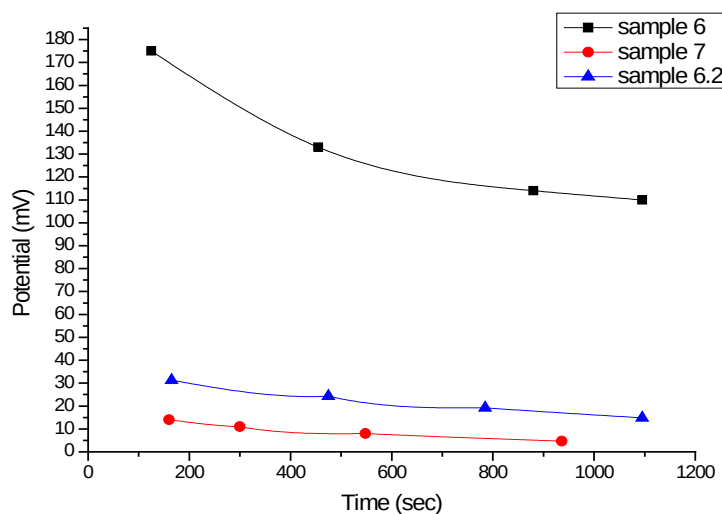


Figure 38. Potential height Pot(t) dependence for Samples #6, #7 and 6.2 (cleavage).

Figure 38 shows comparison of the potential decreasing for different samples under similar conditions: +3 V, 10 sec, room temperature. It is seen that both surfaces of #6 and #7 have same $Pot(t) \sim 1/t$ dependence. Results for “Sample 6.2” (See *Experimental consequence in Section 4.1*) means the results of non-defect surface while the Thermal Module was turned ON. Applied Voltage was even larger [+6 V, 10 sec], however, the measured potential for the scanned area is 6 times smaller. One must note that such Module gave additional noise and affected the resulting values. Still, the tendencies $Pot(t) \sim 1/t$ are similar for all three presented results. Second probability to describe the lowered values is by the impact of the defects on Sample #6. Earlier it was considered to be negligible in our experiments, but defects could partly result into positive outcome on charging. Still it can be justified to be only due the Thermal module noise, however numerical values for charging, limiting potential and relaxation time for Sample #6 presented here were justified to be correctly described.

It can be concluded that the amount of injected charge depends on the applied voltage, time length of charging and the material properties. The relaxation time is 2 h for Sample #6 and nearly 20 min for Sample #7, but it was not be precisely measured due to the low value of $Pot(t)$ for Sample #7 and high noise. After that it is possible to recall at least three other factors, affecting the charges. It is needed to describe the tip form and height (not examined in this work), temperature/pressure conditions, which also cause the additional layer of water molecules [19] and the polarity of applied Potential difference.

5.2.4. Temperature dependence

The NTegra Aura Thermal Mode was applied to investigate the temperature dependence of the charge behavior. It allows heating up to 150 °C in the vacuum conditions. The Sample #6 was prepared for the investigation (See Section 4.1). The average potential of the Sample 6.2 was -0.8 V, which must be taken into account while evaluate the time dependence below. The charging regime [+6 V, 10 sec] was used for temperatures: 30°C, 50°C, 70°C, 90°C, 110°C.

Charging at 30°C is presented on Figure 39 a. Measured $Pot(t)$ is smaller than expected.

It is seen in the Figure 40, that potential is decreasing slightly, as in the previous measurements and showed $Pot(t) \sim 1/t$ dependence. The expected decreasing with temperature is connected to the rise in conductivity and mobility of charges within the dielectric layer. However there is another conflicting effect that should be accounted. When temperature is growing, the layer of the water molecules is getting thinner. The charge leakage

by this chemically adsorbed water film is terminated, thus potential should decrease more slowly.

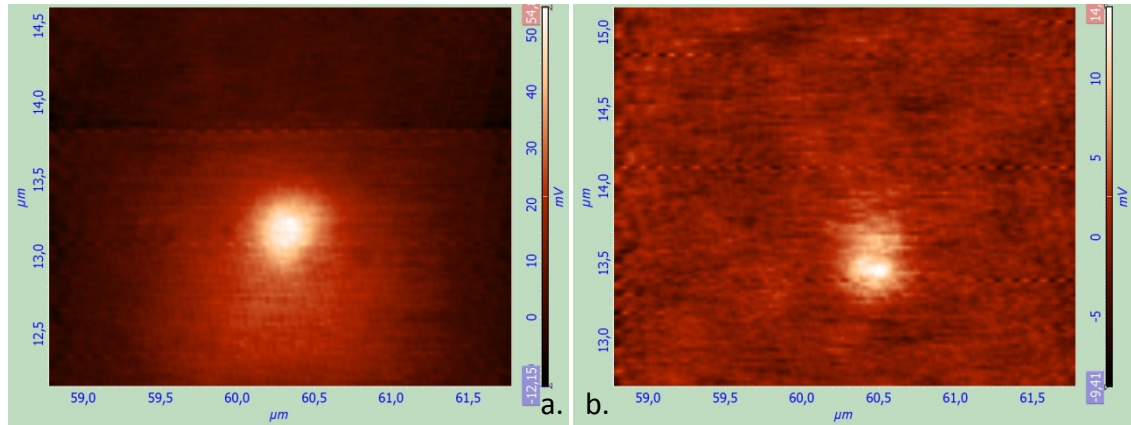


Figure 39. KPFM Surface Potential image of Sample 6.2 after charging [+6 V, 10 sec, 30°C]:

a) $t = 3$ min, Pot = 31 mV; **b)** $t = 17$ min, Pot = 15 mV.

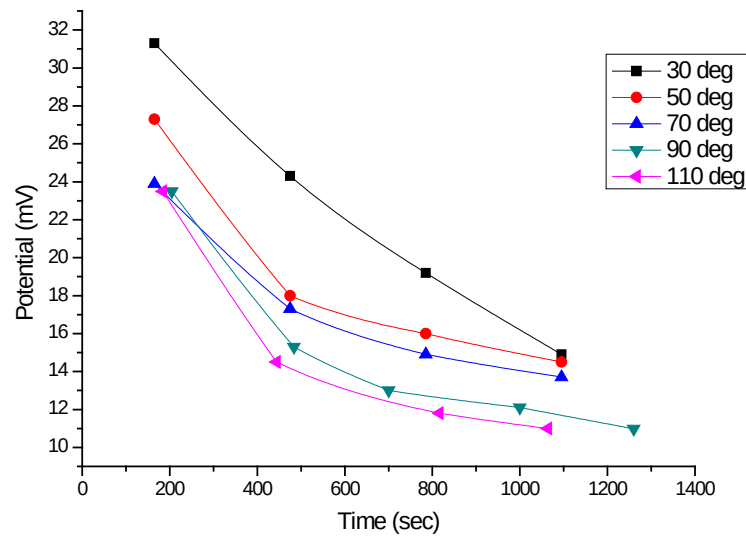


Figure 40. Potential height Pot(t) dependence for different temperature conditions for Sample 6.2 [+6 V, 10 sec].

In the case of the temperature measurements, one more probable effect was found in the surface properties. One can see the complex structure of the potential profile for 30°C (the first measurement) (See Figure 41, which is cross section of Figure 39 a). The potential curve which had the bell shape earlier, here demonstrate the complex shape of two hills, which is not concerned with curvature of the surface, it is the double Gaussian form. Such effect is in accordance with the results for dielectric film with similar composition, LaScO_3 [7, 10].

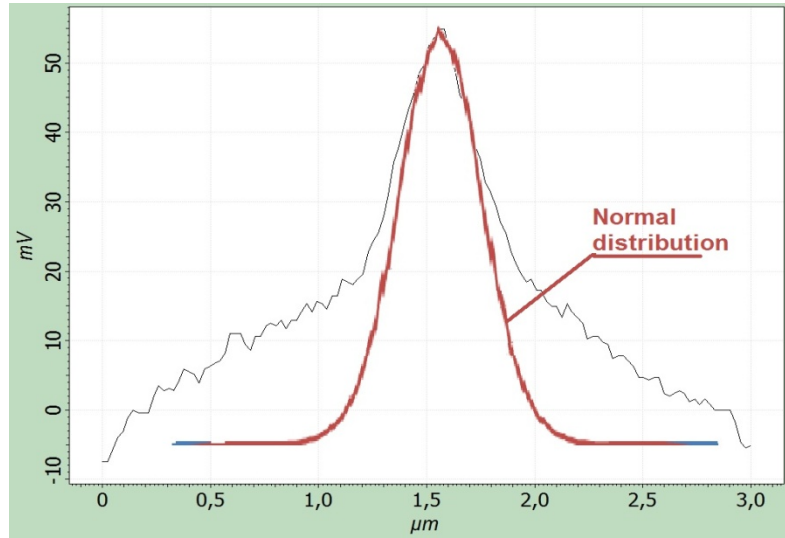


Figure 41. Potential distribution image of Sample 6.2 measured 2 min after charging
[+6 V, 10 sec, 30°C].

Double Gaussian shape can be explained by existence of the interface oxide layer (IL) between LaLuO₃ and Si-wafer. Tunneling into the IL is the reason of second (acclivous) curve, which spreads faster than the first (narrow) curve. Time for this divergence was nearly 10 min. In the Figure 41 is shown the potential distribution profile for Sample 6.2 after two minutes from charging [+6 V, 10 sec, 30°C] with standard Gaussian shape, calculated as Normal distribution. The observed difference can be admitted to the acclivous second Gaussian. This leakage effect should be examined in more details.

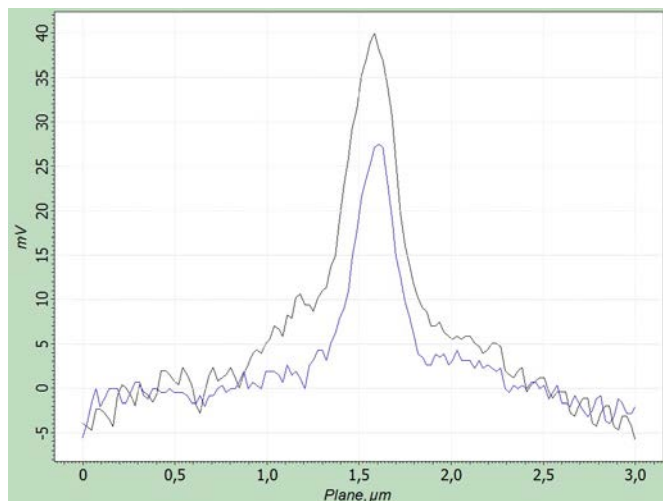


Figure 42. Surface Potential profiles for Sample 6.2 measured 2 min after charging
[+6 V, 50°C] with different lithography duration: 10 sec and 30 sec.

Comparing the results for Sample 6.2 with charging by different durations, widening can be found on the charge profile with increasing the charging length for Sample 6.2 (See Figure 42).

5.2.5. The effect of polarity of charge

While measuring the limiting potential for Sample #7, the difference in heights on the potential profiles was observed (See Figure 43 a, c). The existing own average potential of Sample #7 was negligibly small about -0.02 V, thus it couldn't affect the results.

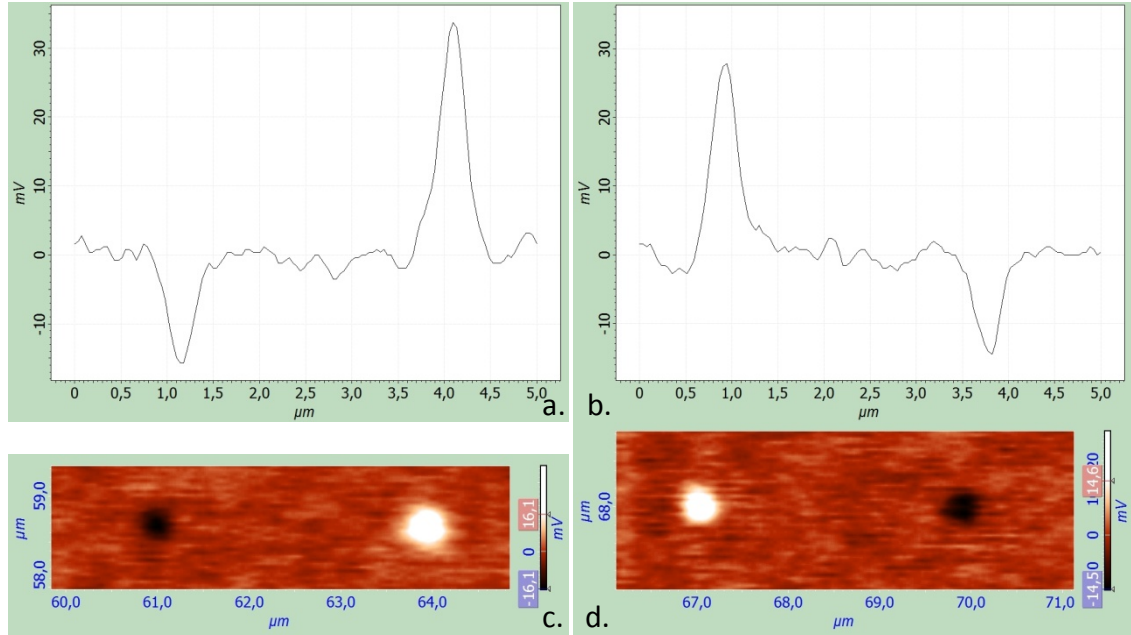


Figure 43. Surface Potential profile for **a.** Charges -7 V, +7 V; **b.** Charges +7 V, -7 V (reversed); Surface Potential images of **c.** Charges -7 V, +7 V; **d.** Charges +7 V, -7 V (reversed).

It can be noted here that for Sample #6 such effect wasn't apparent (See Figure 33), because of the experimental sequence: for the Sample #6 the mentioned series of charged points was prepared for some operating time, assumed as: 10 seconds for charging of every next point and additional 5 seconds for manual switching of modes. According to Figure 27 the dependence of voltage is not absolutely straight: two points are higher (i.e. have larger slope) than the others (See green line on Figure 27). These points are concerned with the positive +1 V and +3 V charging, while blue points are associated with negative voltages: -5 V, -3V, -1 V. Thus, green and blue lines on Figure 27 for Sample #6 reveal dependence of polarity sign.

The polarity effect can be anticipated for both Samples #6 and #7. To prove the effect, we interchanged the applied potential differences: from **-7 and +7** to **+7 and -7** to exclude the factors of the measuring time (See Figure 43 b, d).

Still it was clearly seen that the positive peak is higher than the negative. The charging of the material is easier with the positive applied voltage, than negative. It can be concerned with difference in charge mobility, which should be further determined.

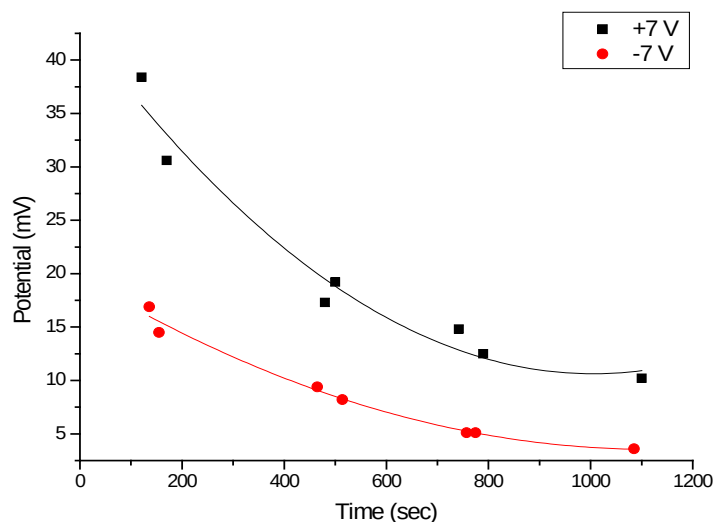


Figure 44. Potential height Pot(t) dependence for different polarity signs for Sample #7.

The results for experiments with Sample #7 are presented in the Figure 44, which shows the appropriate conformity of both measurements. Charging is easier in the case of positive applied potential difference. The *Nova* software allows also calculating the total injected charge (integral of the profile multiplied by the square surface is resulting in the volume of potential), and it has shown 4 times more total value for the positive charging than negative.

5.2.6. Force gradient measurements

The Kelvin Probe Force Gradient Microscopy (KPFM gradient mode) was applied to define the spot size with maximum lateral resolution. As it was told before, KPFGM provides measuring the force gradient by phase angle shift in the degrees. According to our results, the maximum resolution is on the range of 94 nm in experiments of charging the Sample #7 by +3 V 10 sec regime (See Figure 29). A better locality was achieved both by KPFGM and by using thin 20 nm Platinum tips. Resolution better than 250 nm was obtained by charging +7 V 10 sec for Sample #7, which is thought to be nearly 570 nm for standard KPFM mode under the same mentioned charging conditions. Thus it is possible to track the linear approximation for the red line on Figure 29, which will give the result of nearly 25 nm for maximum lateral resolution for KPFGM. This value is in agreement with the level of resolution of KPFGM discussed in literature [27, 47].

The results for Sample #7 charging series of three points [+7 V, 10 sec] are presented on the Figure 45, which was preliminary processed by uniform transformation in *Nova image Analysis*.

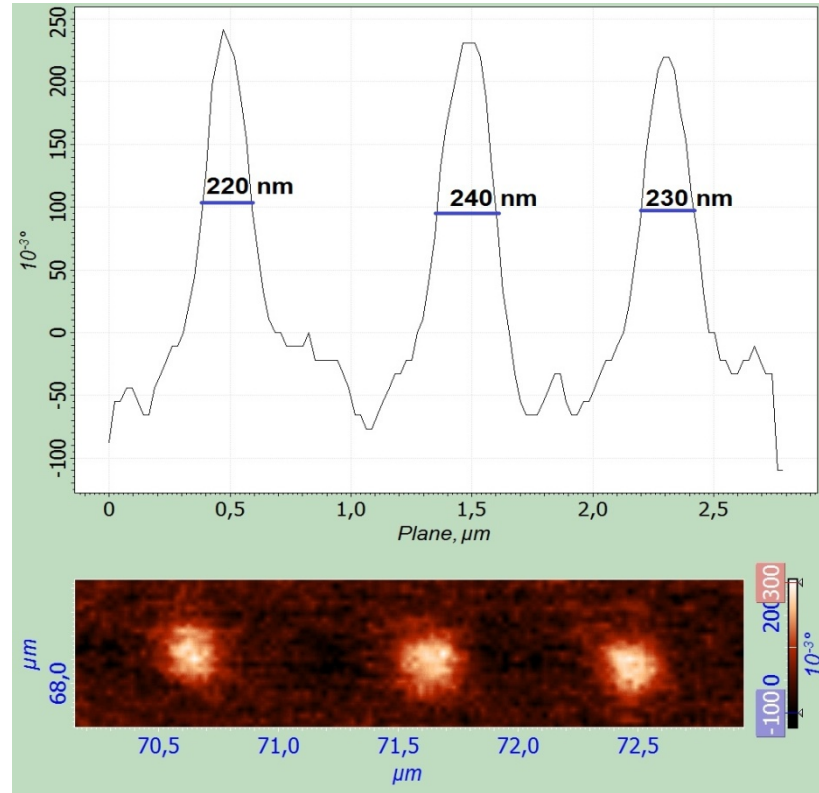


Figure 45. Potential profile and KPFGM image of charged [+7 V, 10 sec] series for Sample #7.

Still, the better lateral resolution doesn't allow to speculate the certain values for potential of the spots and mainly KPFGM-AM was used in our study. However it's possible to think of the charge values in degrees and track down the Potential height time dependence similar to the presented above for KPFGM: $\text{Pot}(t) \sim 1/t$. Special programs for these transforms can be used.

The large noise level didn't allow to find the actual size of the spots L required for calculation of mobility, diffusion coefficient and activation energy.

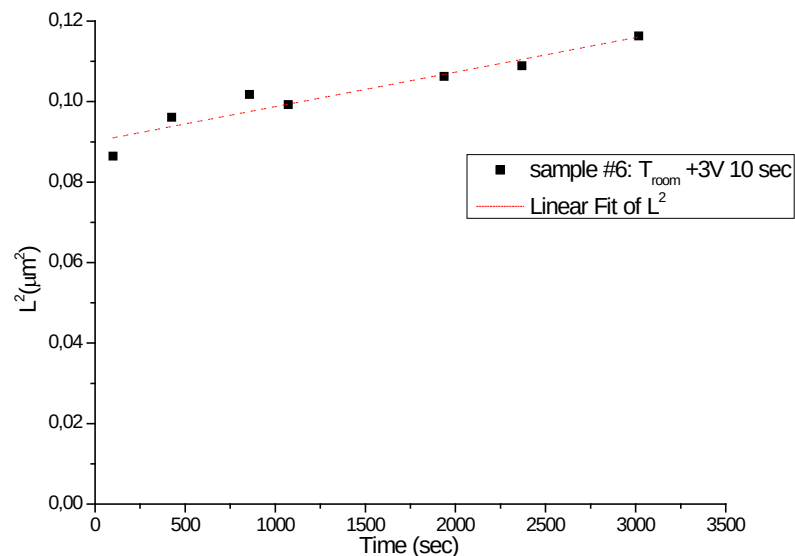


Figure 46. Experimentally obtained dependence of $L^2(t)$ of charge for Sample #6 [+3 V, 1 sec].

Nonetheless it is possible to evaluate the order of diffusion coefficient D from the Diffusion law $L^2 = D \cdot t$ by considering $L \approx \text{FWHM}$. Diffusion coefficient D is the slope of $L^2(t)$ seen in Figure 46. It is measured to be nearly $8.5 \cdot 10^{-10} \text{ cm}^2/\text{sec}$. From the Einstein-Smoluchowski relation for charges: $D = \mu \cdot k_B \cdot T / q$. Mobility μ can be estimated as $4 \cdot 10^{-10} \text{ cm}^2/(\text{V} \cdot \text{sec})$. The values are in accordance by order for similar semiconductor LaScO_3 found in literature [7, 10]. Still it wasn't possible to precisely define the size of the charge spots for different temperature conditions (in Section 5.2.4), which is necessary for defining the activation energy E_A from the prescribed Arrhenius law $D = D_0 \cdot \exp(-E_A/k_B T)$.

5.3. Nanolithography observations

Considering the material's property to store the injected charge for rather long period of time, Nanolithography was tested on practical raster image. The raster sample - logo of the Lappeenranta University of Technology, similar to the symbol "&" - was drawn in the $8 \mu\text{m}$ variant on the surface of Sample #6 (See Figure 47). The applied Voltage range was -5 V to 0 V, thus injected charge was negative to the background.

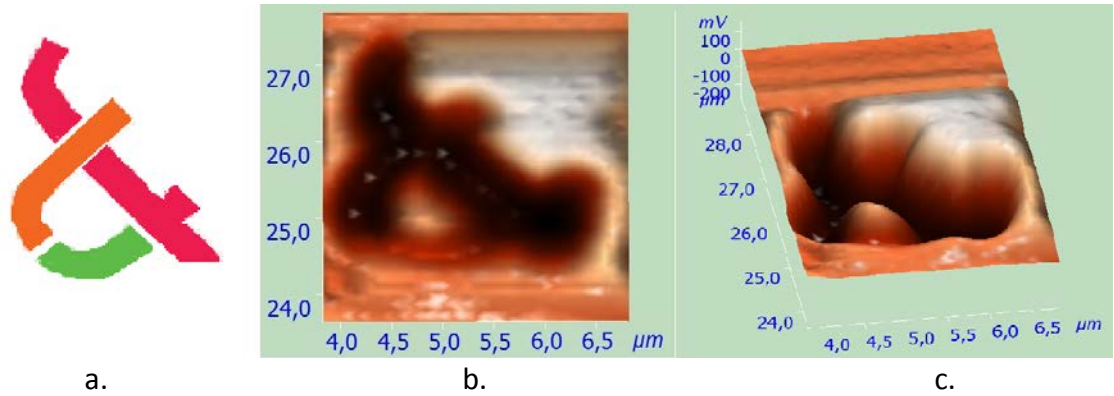


Figure 47. Charge nanolithography in Sample #6. **a.** Starting raster sample image;
b. Image of the logo $2.5 \times 2.5 \mu\text{m}^2$. Light area is 0 V, dark area is -5 V;
c. 3D-reconstruction image of the LUT logo.

The color gradation was not apparent for four supposed voltages. To obtain better resolution and recognition, it was needed to consider the effect of polarity. While the positive charge is injected easier than the negative, the positive potential difference should be associated with the symbol, but not with the background. Thus, using the inversed (negative) lithography sample and larger lateral scale the symbol become recognizable (See Figure 48).

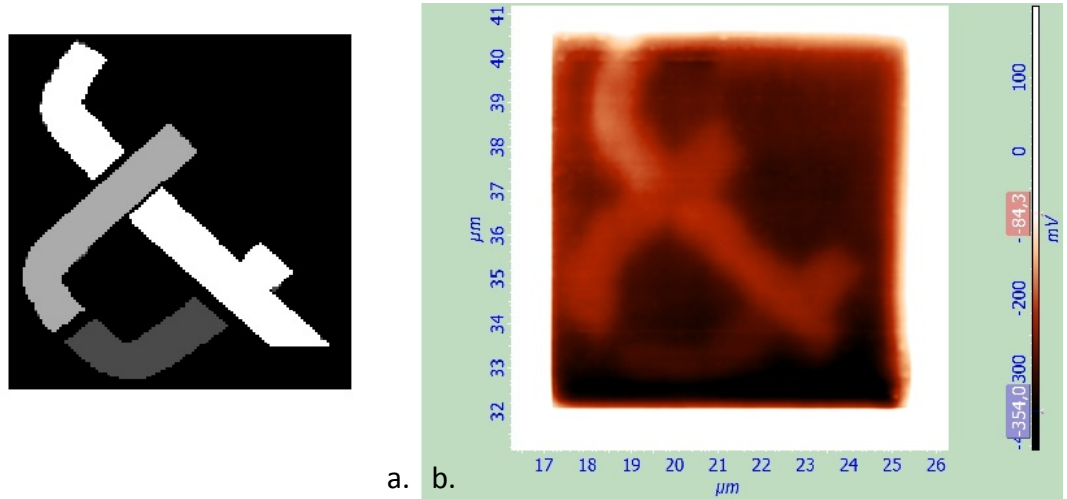


Figure 48. Charge nanolithography in Sample #6. **a.** Negative Sample;
b. Surface Potential image of the logo $8 \times 8 \mu\text{m}^2$. Light area is 0 V, dark area is -5 V.

The charge was keeping its shape for a period of few minutes. It can be noted, that special techniques of sample correction should be used in lithography of charge, as well as photomask correction is performed in Photolithography.

Demonstration of lithography by charging the points in LaLuO_3 thin films is a qualitative and visible proof of the possibilities of NTegra Aura system, KPFM mode and the remarkable properties of the investigated dielectric for Nanolithography.

Conclusions

- 1) AFM studies of surface topography indicated smooth and uniform surface of both 6 nm and 25 nm thick samples. The surface inhomogeneities have range of 2 nm.
- 2) Structural artifacts were found in sample of thickness 6 nm (obtained by MBE technique) by the Surface Potential studies in KPFM mode. The objects were up to 2 μm in diameter, had an ellipse shape and consisted of negatively charged core with potential of -30 mV and positively charged elongated cloud area with +140 mV. The background noise in KPFM was nearly 4 mV.
- 3) Samples of LaLuO_3 are capable for the charge lithography, though their susceptibility to the applied potential differs in more than three times. At room temperature and medium vacuum conditions, value of the measured potential growth for +3 V was at level of 200 mV for 6 nm thick film, while for 25 nm thick film the growth was nearly 50 mV. This can be corresponded to the 4-fold distinction in sample width due to the formula $E \sim U/d$.
- 4) Lateral resolution for samples in KPFM with tungsten tips had range of 350 nm, the application of thin platinum tips with radius of 20 nm increased resolution only up to 250 nm.
- 5) Lateral resolution of nearly 100 nm was achieved in KPFM gradient mode with thin platinum tips, while maximum achievable resolution was estimated to be nearly 25 nm. Therefore, KPFGM is more preferable for dimensional studies of area with injected charge.
- 6) Lateral size of the charged area was broadening with time as $t^{0.5}$, i.e. in accordance with the Diffusive model of charge spreading. In the first 10 min the injected charge is leaking from the film to the substrate, which is revealed as decrease of the total charge Q and the existence of double Gaussian shape on surface potential profile in first measurements, which is in accordance to the data for the similar materials in literature. Tunneling into the interface layer was established as the reason of partial decrease in total charge in LaLuO_3 dielectric thin films.
- 7) Relaxation time for 6 nm thick sample is nearly 2 hours, while for the 25 nm sample it is nearly 20 minutes. The potential level is decreasing proportionally to $1/t$.
- 8) Charging time affects the size and the form of the surface profile. Increasing of the charging duration lead to wider spot size, bigger value of potential and thicker Gaussian shape. Temperature exposure decreases the potential which is caused by rise in mobility of charge carriers. The influence of charging time and temperature effect can also be attributed to the Tunneling of charge and Diffusive model of charge dissipation.

9) A polarity effect was found for LaLuO_3 , which is in contradiction with the literature data for similar dielectric materials. It was determined that for LaLuO_3 charge is more than in two times easily injected by application of positive potential difference. This fact may be explained by distinction in mobilities of charge carriers, but in any case the results for impact of polarity should be further verified.

10) Influence of ambient pressure and moisture conditions was established. Depressed atmosphere is causing the decrease of water layer thickness and contributes to the charge retention and retardation of the potential decrease, which was demonstrated in the temperature measurements for 6 nm thick sample.

11) At the same time LaLuO_3 has shown high sustainability of injected charges in common room conditions. It was demonstrated that after the device was devacuumized for 3 hours, such room air and moisture exposure was followed by detection of charge still remaining in the surface of dielectric layer for 6 nm sample.

12) Morphological difference between the two high-k coatings, obtained by MBE and PLD techniques, was determined. 25 nm film made by PLD possesses better structural characteristics of surface uniformity, which is compulsory for industrial applications. Concurrently, the 6 nm sample obtained by MBE method had structural defects and the increased capabilities for injection and reservation of charge for Nanolithography.

Summary

In this work LaLuO_3 was investigated for the surface potential mapping by Kelvin probe microscopy for the first time. Results for high resolution AFM measurements of surface morphology are also demonstrated. For this purposes the methodology of Scanning Probe Microscopy measurements was developed on practice. Measurements were conducted using multifunctional NT-MDT NTegra Aura system, providing opportunity to study samples in vacuum.

The main highlights of this work can be established:

- 1) By comparing the KPFM and enhanced KPFGM techniques, lateral resolution 300 nm and 100 nm respectively was obtained for LaLuO_3 films.
- 2) The potential profile height is falling down proportionally to $1/t$. Concurrently, the charged spots were widening proportional to $t^{0.5}$. The total charge Q is leaking into the interface layer during first 10 min, after that Q do not change. At the same time with the complex shape of potential profile the dominant mechanism of diffusion was established for charge dissipation.
- 3) The order for values of diffusion coefficient is $10^{-9} \text{ cm}^2/\text{sec}$, the order for mobility is $10^{-10} \text{ cm}^2/(\text{V}\cdot\text{sec})$.

These values are significant for comprehensive studies and comparing of high-k dielectric materials, they can be used to develop the technology of IC.

The establishing of the polarity effect should be emphasized. By applying the positive voltage the total charge is nearly 4 times more stored and three times easily injected.

In this Master's Thesis the chargeability parameter was introduced for convenience, few original pictures were created to demonstrate the occurring phenomena. For visibility issues, the data was presented in graphs instead of numerical tables. The consequence of the study was declared in advance and then followed. Thereby the general methodology integrated into this study resulted in the conclusions of quantitative and qualitative criterions of future prospects for LaLuO_3 dielectric films. In purposes of methodical interest of this study, the sequence of experiments was presented step by step, with system functions described and the certain parametrical values for settings were given.

The definite numerical parameters can be further used for investigations of surface properties and for verification of the results.

Few important weaknesses must be called for this research. Some shortcomings are associated with the mentioned restrictions and could be evaded by inclusion of more functional measuring systems. In particular, the numerical values for surface potential measurements should be perceived with discretion, because the applied Thermal Module was causing high level of interference noise. Mainly it was eliminated by using the *Nova* software for image processing and the Fourier transforms. Presumably the noise was caused by grounding and lowered the potential values. Nevertheless, the trend of potential drop is consistent with the results of all the other experiments, thus it was justified to be correct.

The model describing charge behavior in view of Tunneling into the interface layer should be overlooked with strong attention. In some models, the charge is leaking into the oxide layer between semiconductor and silicon wafer, and only after that it is spreading by the diffusion mechanism. Obtained results have shown constancy of spot size in time for some conditions.

The used tips did not allow the voltage more than 10 V. In future studies seems reasonable to use blunt tips with lower resistivity for charge limit investigations.

The water layer affected the losses of total charge, because medium vacuum is not enough to dry the surface properly. Inert gases atmosphere, high vacuum and heating (at least 350 deg) are required to thoroughly dry the surface. This can be implemented in more enhanced devices. However it was found that even medium vacuum conditions increase the Quality factor of the probes for the experiment in more than 50 times.

In terms of the experiment, it would be worth to implement the line charging rather than point charging, which is more relative to the actual industrial memory devices. Nevertheless, the objective factors of measured potential decrease and charge spreading do not depend on such form. Also the experiments aimed to determine the engineering parameter of capacitance equivalent thickness (CET) associated with the relative value of dielectric constant supposed to be carried out.

It is worth noting that at the time of using the device, few remarkable details were found on practice, while attention to those is not clearly emphasized in the literature. For example, the sample drift, caused by impact of the needle probe and thermal expansion had maxima as 5 micron per hour. Also noted: the existence of the wave front of charge divergence on the first scans, non ordinary influence of structural defects on the properties of the sample, as well as fragility and specific imperfections of the probe tips.

Finally, on the basis of the results along with review of literature related to the issue of Kelvin probe microscopy, few possible ideas for further research can be named:

- 1) All the previously mentioned shortcomings should be eliminated. Especially errors in the measurement of time.
- 2) Limitations of the measuring system can be overcome by using a more advanced device. Thus ranges of exposure might be expanded: vacuum, heating/cooling, moisture content, voltage etc. Also it can be possible to measure the mechanical characteristics, e.g. adhesion and stiffness, which is possible in advanced systems.
- 3) Study the impact of the surface water layer and its properties, e.g. Newtonian properties, also in case of ionic and viscous fluids. The forces occurring might be valuable in description of SPM operation in different modes and Nanolithography of charge.
- 4) Study the impact of electromagnetic radiation on the LaLuO_3 surface potential properties and lithography, both in cases of dark/light conditions.
- 5) Using the developed methodology seems meaningful to study various classes of structures: QDs, photovoltaics in light/dark, fiber materials, penometals, polymers, even biological structures such as living cells.
- 6) To develop the computational methods of data analysis for different SPM modes and conditions for more precise and automatic application. For example, to use different ranges of tip-sample interaction force, which is still developed in devices nowadays.
- 7) Use more functional programs for image and data analysis and develop the processing software to compare the materials suitable for high-k application.

The listed studies and development of experimental system may provide fundamental value and can be used to improve the existing technologies.

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Appendice I. List of Figures

Figure 1. MOSFET and flash memory constructions.

Figure 2. Experimental scheme of charge measurements by AFM.

Figure 3. Types of Scanning Probe Microscopy. Family of KPM methods.

Figure 4. Operational principle of AFM.

Figure 5. Lennard-Jones potential: equation and curve.

Figure 6. Scheme of scanning process in SPM.

Figure 7. AFM Constant force and Constant distance modes with topography.

Figure 8. Distance in Semicontact mode. Three principles of AFM modes.

Figure 9. Scheme of the cantilever with tip in forced movement.

Figure 10. SEM image of NN-T190-HAR5 tips: radius = 50 nm, angle = 12°.

Figure 11. Major mechanical modes of tip's bending vibrations.

Figure 12. Operational principle of piezo scanner's tube movement.

Figure 13. Piezo ceramic disadvantages: a. nonlinearity; b. creep; c. hysteresis.

Figure 14. Simplified scheme of the feedback working principle and photo detector.

Figure 15. Algorithm of processing the relative measurement by closest 8 points.

Figure 16. Demonstration of AFM tip used for KPFM and Kelvin Probe.

Figure 17. Comparison between Amplitude Modulation and Frequency Modulation modes.

Figure 18. NTegra Aura device without the vacuum hood.

Figure 19. Roadmap of EFM family by 2006.

Figure 20. Experimental facility scheme and device used for MBE.

Figure 21. Working window of the Nova program.

Figure 22. The raw image obtained for Surface Potential.

Figure 23. Image revealing artifacts caused by the excess value of lift height.

Figure 24. The Nova Image Analysis main window.

Figure 25. The 3D-recovery of surface topography for sample #6 with artifact on the right.

Figure 26. Mag(z) curve to define the Driving distance value in Semicontact Mode.

Figure 27. Electrical chargeability of Samples #6 and #7.

Figure 28. KPFM results for Sample #6 after charging [+3 V, 10 sec].

Figure 29. FWHM vs. Voltage dependence for Sample #6 (KPFM) and Sample #7 (KPFGM).

Figure 30. Surface Potential for ellipse shaped defects in Sample #6. Mapping and Profile.

Figure 31. Surface Potential for defects after charging [+3V, 10 sec]. Mapping and Profile.

Figure 32. 3D-reconstruction of the surface defect found in KPFM Surface Potential.

Figure 33. Surface Potential image of a charged series for Sample #6, charging duration 10 sec.

Figure 34. Surface Potential profile for the series of charges.

Figure 35. Surface Potential image of a charged series by duration. Charging voltage +3V.

Figure 36. Potential height Pot(t) dependence for different charging duration for Sample #6.

Figure 37. KPFM Surface Potential image of area after 3 hours on atmosphere (Sample #6).

Figure 38. Potential height Pot(t) dependence for Samples #6, #7 and 6.2 (cleavage).

Figure 39. KPFM Surface Potential image of Sample 6.2 after charging [+6 V, 10 sec, 30°C].

Figure 40. Potential height Pot(t) dependence with temperature for Sample 6.2 [+6 V, 10 sec].

Figure 41. Potential distribution image of Sample 6.2, 2 min after charging [+6 V, 10 sec, 30°C].

Figure 42. Surface Potential profiles for Sample 6.2, 2 min after charging [+6V, 50°C] 10, 30 sec.

Figure 43. Surface Potential profiles and images for charges [-7 V, +7 V] and reversed position.

Figure 44. Potential height Pot(t) dependence for different polarity signs for Sample #7.

Figure 45. Potential profile and KPFGM image of charged [+7 V, 10 sec] series for Sample #7.

Figure 46. Experimentally obtained dependence of $L^2(t)$ of charge for Sample #6 [+3 V, 1 sec].

Figure 47. Charge nanolithography in Sample #6: raster sample, litho image, 3D-reconstruction.

Figure 48. Charge nanolithography in Sample #6. Negative sample and Surface Potential image.

Appendix II. History of SPM

Table 1. SPM techniques and capabilities

SPM techniques and capabilities	
1	Scanning tunneling microscope (1981) —G. Binnig, H. Rohrer —Atomic resolution images of conducting surfaces
2	Scanning near-field optical microscope (1982) —D. W. Pohl —50 nm (lateral resolution) optical images
3	Scanning capacitance microscope (1984) —J. R. Matey, J. Blanc —500 nm (lateral resolution) images of capacitance variation
4	Scanning thermal microscope (1985) —C. C. Williams, H. K. Wickramasinghe —50 nm (lateral resolution) thermal images
5	Atomic force microscope (1986) —C. Binnig, C. F. Quate, Ch. Gerber —Atomic resolution on conducting/non-conducting surfaces
6	Scanning attractive force microscope (1987) —Y. Martin, C. C. Williams, H. K. Wickramasinghe —5 nm (lateral resolution) non-contact images of surfaces
7	Magnetic force microscope (1987) —Y. Martin, H. K. Wickramasinghe —100 nm (lateral resolution) images of magnetic bits/heads
8	“Frictional” force microscope (1987) —C. M. Mate, G. M. McClelland, S. Chiang —Atomic-scale images of lateral (“frictional”) forces
9	Electrostatic force microscope (1987) —Y. Martin, D. W. Abraham, H. K. Wickramasinghe —Detection of charge as small as single electron
10	Inelastic tunneling spectroscopy STM (1987) —D. P. E. Smith, D. Kirk, C. F. Quate —Phonon spectra of molecules in STM
11	Laser driven STM (1987) —L. Arnold, W. Krieger, H. Walther —Imaging by non-linear mixing of optical waves in STM
12	Ballistic electron emission microscope (1988) —W. J. Kaiser (1988) —Probing of Schottky barriers on a nanometer scale
13	Inverse photoemission microscope (1988) —J. H. Coombs, J. K. Gimzewski, B. Reihl, J. K. Sass, R. R. Schlittler —Luminescence spectra on nanometer scale
14	Near-field acoustic microscope (1989) —K. Takata, T. Hasegawa, S. Hosaka, S. Hosoki, T. Komoda —Low frequency acoustic measurements on 10 nm scale
15	Scanning noise microscope (1989) —R. Moller, A. Esslinger, B. Koslowski —Tunneling microscopy with zero tip-sample bias
16	Scanning spin-precession microscope (1989) —Y. Manassen, R. Hamers, J. Demuth, A. Castellano —1 nm (lateral resolution) images of paramagnetic spins
17	Scanning ion-conductance microscope (1989) —P. Hansma, B. Drake, O. Marti, S. Gould, C. Prater —500 nm (lateral resolution) images in electrolyte
18	Scanning electrochemical microscope (1989) —O. E. Husser, D. H. Craston, A. J. Bard
19	Absorption microscope/spectroscopy (1989) —J. Weaver, H. K. Wickramasinghe —1 nm (lateral resolution) absorption images/spectroscopy
20	Scanning chemical potential microscope (1990) —C. C. Williams, H. K. Wickramasinghe —Atomic scale images of chemical potential variation
21	Photovoltage STM (1990) —R. J. Hamers, K. Markert —Photovoltage images on nanometer scale
22	Kelvin probe force microscope (1991) —M. Nonnenmacher, M. P. O’Boyle, H. K. Wickramasinghe —Contact potential measurements on 10 nm scale
23	Apertureless near-field optical microscope (1994) —F. Zenhausern, M. P. O’Boyle, H. K. Wickramasinghe —Optical microscopy at 1 nm resolution

Appendix II (continued). Future technologies

(taken from [40] S.Morita - Roadmap for Scanning Probe Microscopy 2006)

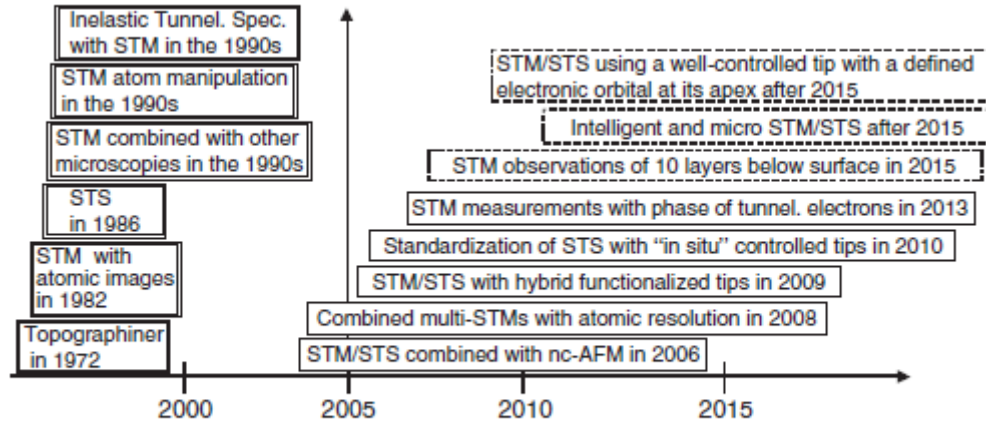


Fig. 2.3. Roadmap of STM

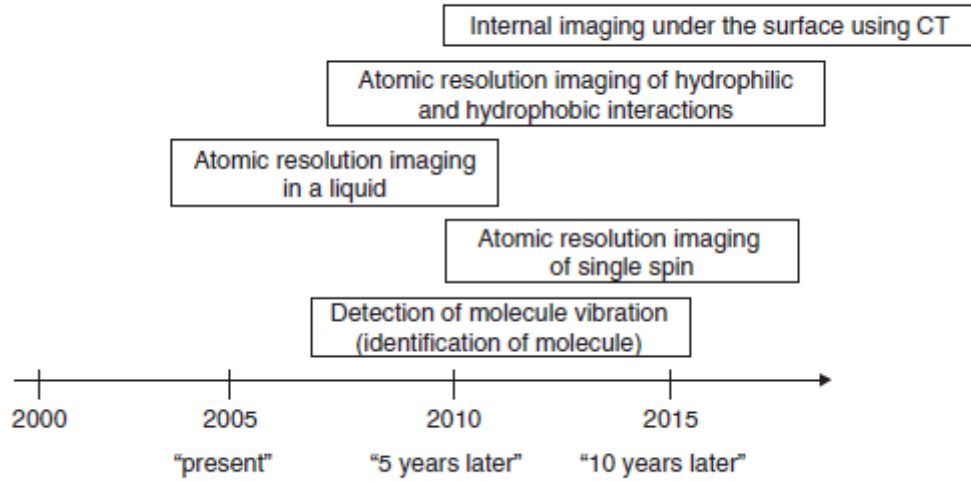


Fig. 3.6. Future predictions for novel AFM techniques